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THE STRUCTURE OF THE SUBSTANCES OBTAINED BY THE ADDITION OF ORGANIC OXYGEN COMPOUNDS AND ALUMINIUM HALIDES.

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It is well known that the halogen compounds of aluminium combine with many organic compounds and that the resulting addition-products play an important part in some of the reactions in which aluminium compounds are used as catalysts. Very little is known, however, about the properties of these products, and there is no experimental basis for the structural formulas that have been proposed for them. The object of the experiments described in this paper was to ascertain whether the composition and properties of an important class of these addition-products can be represented by valence formulas and whether there is any relation between these substances and salts with water of crystallization.

That aluminium halides combine with organic oxygen compounds was discovered by Gustavson,[1] who found that aluminium chloride combines with ethyl benzoate to form a

[1] Ber. d. chem. Ges., 13, 157.

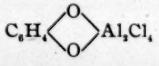
substance whose composition is represented by the formula

$$AlCl_3.C_6H_5COOC_2H_5.$$

Shortly afterwards Combes[1] obtained a substance with the composition $AlCl_3.C_6H_7O_3$ as one of the products of the reaction between aluminium chloride and acetyl chloride, and Winogradoff,[2] working under Gustavson, obtained the substance $C_4H_4O_2Cl.AlCl_3$ as a second product of the same reaction. Later, Louise and Perrier[3] succeeded in isolating a crystalline substance with the composition

$$AlCl_3.C_6H_3(CH_3)_3COC_6H_5,$$

from the products of the reaction between aluminium chloride, mesitylene, and benzoyl chloride. This led Perrier[4] to undertake a systematic study of the reaction between aluminium chloride and organic oxygen compounds. Perrier found that aluminium chloride combines with acid chlorides, ketones, esters, phenols, borneol, and camphor. Of the addition-products obtained by Perrier, the most interesting are those with acid chlorides and ketones, since they represent successive stages in the synthesis of ketones by the Friedel and Crafts reaction. It is doubtful whether the compounds with phenols are formed by direct addition, as claimed by Perrier, since Claus and Mercklin[5] found that hydrochloric acid is evolved when aluminium chloride and phenols are brought together in an indifferent medium. To the product of the reaction between aluminium chloride and resorcinol they give the formula



instead of the formula

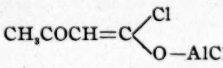
$$C_6H_4(OH)_2.Al_2Cl_6$$

given by Perrier.

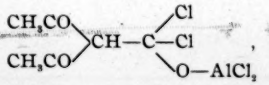
All the addition-products of organic oxygen compounds and aluminium chloride that have hitherto been analyzed, with the

[1] Ann. chim. phys., [6], **12**, 199.
[2] J. prakt. Chem., [2], **37**, 110.
[3] Compt. rend., **114**, 1377.
[4] *Ibid.*, **116**, 1140; **116**, 1298; **119**, 276.
[5] Ber. d. chem. Ges., **18**, 2934.

exception of the doubtful compounds with phenols, have the same general composition. They contain 1 molecule of an organic compound, which has at least one doubly-linked oxygen atom, in combination with 1 molecule of aluminium chloride. It is natural to assume, therefore, that this doubly-linked oxygen atom is in some way connected with the existence of the substances, and all the structural formulas that have been proposed for them are based on this assumption. For the substance prepared by Winogradoff, Gustavson[1] wrote the formula

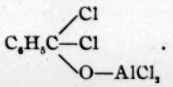


without offering any experimental evidence in its favor, and to the substance obtained by Combes he gave the formula



since he assumed that it was formed from the former by addition of acetyl chloride.

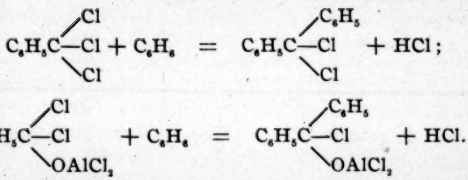
Kronberg[2] has recently proposed similar formulas for the addition-products of aluminium chloride and acid chlorides. For the compound with benzoyl chloride, for example, he suggests the formula



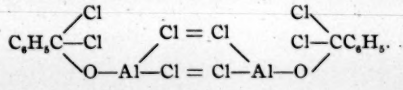
Kronberg uses this formula to account for the mechanism of the Friedel and Crafts reaction that was proposed, independently, by Perrier[3] and Boseken.[4]

The only evidence offered in favor of the formula is based on the analogy between benzotrichloride and the benzoyl chloride addition-product, as illustrated by the following equations :

[1] J. prakt. Chem. [2], **37**, 109.
[2] *Ibid.*, [2], **61**, 494.
[3] Compt. rend., **116**, 1300.
[4] Rec. trav chim. Pays-Bas, **19**, 19.



In a paper on the molecular weight of aluminium compounds[1] I showed that these addition-products have double the molecular weight that is usually assigned to them, and that the two halves of the molecules are linked together by the halogen atoms derived from aluminium chloride. This fact may be represented by writing the Gustavson-Kronberg formula,



This formula can be tested by experiment. If it is correct, then only those oxygen compounds which have at least one doubly-linked oxygen atom can combine with aluminium chloride. The results described in this paper show that this is not the case, since ethers of all kinds combine with aluminium chloride and aluminium bromide. The products are crystalline substances whose composition and molecular weight are represented by the formula $(R_2O.AlX_3)_2$. They are, in every respect, exactly like the corresponding substances obtained from acid chlorides and ketones. The formulas of Gustavson and Kronberg are, therefore, wrong.

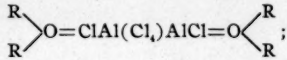
This leaves two possibilities: either these addition-products contain oxygen that has a higher valence than two, or else their formation does not depend upon the oxygen atoms in the organic substance. If the former is true, then the composition of the addition-products ought to vary with the number of oxygen atoms in a molecule of the organic compound. It is difficult to test this with aluminium chloride because of its insolubility in liquids that do not combine with it; but the

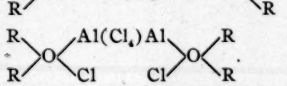
[1] This JOURNAL, 24, 385.

results obtained with aluminium bromide are conclusive. It was found that the addition-products, with substances that have 1 atom of oxygen to the molecule, invariably contain 2 molecules of the oxygen compound to 1 "double" molecule of aluminium bromide, while the addition-products obtained from substances that have two atoms of oxygen generally contain only one molecule of the organic compound to one double molecule of aluminium bromide.

Terephthalyl chloride, for example, forms the compound $Al_2Br_6.C_6H_4(COCl)_2$, while the corresponding mono-acid chloride forms $Al_2Br_6.2C_6H_5COCl$. Similarly, diacetylmesitylene forms $Al_2Br_6.C_6H(CH_3)_3(COCH_3)_2$, while the corresponding mono-ketone combines with one-half as much of the bromide to form the compound $Al_2Br_6.2C_6H_3(CH_3)_3COCH_3$. These cases, and many similar ones, show that a substance that contains 2 atoms of oxygen to the molecule can combine with twice as much aluminium bromide as a substance that contains but one. The combination, therefore, probably takes place through oxygen.

All the facts that have been presented can be represented by the following formulas:

I.  ;

II.  .

Formula I. is not in harmony with the behavior of many of the addition-products when they are heated. Acetylacetone, for example, combines with aluminium bromide to form a compound with the composition $Al_2Br_6.2C_5H_8O_2$. This decomposes at ordinary temperatures according to the equation

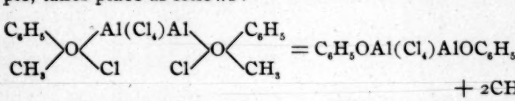
$$Al_2Br_6.2C_5H_8O_2 = Al_2Br_4.2C_5H_6O_2 + 2HBr.$$

The product of this decomposition combines with more acetylacetone, forming a new addition-product which also decomposes on heating, and the process of addition and decomposition can be repeated until the final product is pure

aluminium acetylacetone—a substance analogous to aluminium hydroxide. The addition-products with ethers and phenols behave in the same way. Thus, Hartmann and Gattermann[1] found that the substance, $Al_2Cl_6.2C_6H_5OCH_3$, decomposes at 120° according to the equation

$$Al_2Cl_6.2C_6H_5OCH_3 = Al_2Cl_4.2C_6H_5O + 2CH_3Cl,$$

and Merz and Weith[2] found that when aluminium chloride is heated with phenol the final product is aluminium phenolate. All of these reactions are easily understood, if the structure of the addition-products is represented by formula II. The decomposition of the double compound with anisol, for example, takes place as follows:



It is remarkable that 1 molecule of an aluminium halide never combines with more than 2 molecules of an organic oxygen compound while it combines with 6 molecules of an aromatic hydrocarbon.[3] Since many of the colored addition-products described in this paper change color when dissolved in benzene, it is probable that these substances also combine with aromatic hydrocarbons. After many attempts at isolating such addition-products I finally succeeded with anthraquinone, which forms the compound $Al_2Br_6.C_{14}H_8O_2.2C_6H_6$. This suggests, as a possible explanation of the Friedel and Crafts reaction, that the aluminium halide combines with both the acid chloride and the hydrocarbon, forming a complex molecule which subsequently undergoes a rearrangement similar to that observed in the case of the addition-product with acetylacetone. Such a mechanism would explain why the reaction takes place only with aromatic hydrocarbons.

It has been found, quite recently, that the composition and properties of a number of substances can be explained by the assumption that they contain quadrivalent oxygen. Since

[1] Ber. d. chem. Ges., **25**, 3531.
[2] *Ibid.*, **14**, 189.
[3] Gustavson: Jour. Russ. Phys. Chem. Soc., **10**, 305.

most of these substances have been obtained by the addition of acids to organic oxygen compounds, Baeyer and Villiger assume that quadrivalent oxygen has basic properties and that the substances are oxonium salts analogous to ammonium salts. There seems to be no difference between the addition of acids, described by Baeyer and Villiger, and that of salts described in this paper. The substances that combine with the former also combine with the latter, and the resulting addition-products resemble each other so closely that it is impossible to distinguish between them except by chemical methods. This is true, for example, in the case of dibenzalacetone. Baeyer and Villiger[1] conclude that the compound, $(C_6H_5CH{=}CH)_2CO.HCl$, cannot be a chlorhydrine because it is red, while the ketone chloride, $(C_6H_5CH{=}CH)_2CCl_2$, is colorless. Dibenzalacetone combines with aluminium halides as readily as it does with hydrochloric acid, and the resulting addition-products have the same brilliant red color that first drew attention to the compound with hydrochloric acid. The same relations hold in the case of a number of substances which dissolve in acids to form highly-colored solutions. Thus, the unsaturated ketones combine with aluminium bromide to form substances whose color is red; xanthone, which is pale-yellow in color, and methylenephenylene ether, which is colorless, dissolve in concentrated sulphuric acid to form intensely yellow solutions and combine with aluminium halides to form compounds which have the same color as the acid solutions. There can be very little doubt that the addition-products of organic oxygen compounds with acids and those with salts like the aluminium halides have the same structure.

EXPERIMENTAL PART.

I. Compounds with Ethers.

The aluminium halides combine with aliphatic ethers with evolution of heat. The products are either liquids or very finely divided solids, which are almost impossible to wash and dry without serious decomposition. For this reason only the

[1] Ber. d. chem. Ges., 34, 2639.

crystalline compounds with aromatic ethers were purified and analyzed.

1. Phenyl Ether and Aluminium Bromide, $Al_2Br_6.2(C_6H_5)_2O$. —Aluminium bromide dissolves in phenyl ether with evolution of heat, but it is difficult to isolate a pure substance from the solution. It is better to bring the substances together in carbon disulphide solution and precipitate the product with low-boiling petroleum ether. If the ether is carefully stratified on top of the solution the product crystallizes slowly in large lemon-yellow plates that are easily purified. The preparations used in the following experiments were washed with a mixture of petroleum ether and carbon disulphide and dried in a current of dry air.

To determine the amount of phenyl ether contained in the substance, a weighed quantity of the latter was decomposed with ice, the resulting liquid extracted with pure ether, the ethereal solution dried with a little fused calcium chloride, and evaporated in a weighing tube. The aluminium was determined as oxide by decomposing a weighed quantity with ice-water, evaporating the solution, and igniting the residue.

I. 1.6409 grams substance gave 0.6449 gram $(C_6H_5)_2O$.
II. 0.7265 gram substance gave 0.0850 gram Al_2O_3.

	Calculated for $Al_2Br_6.2(C_6H_5)_2O$.	Found. I.	Found. II.
$(C_6H_5)_2O$	38.91	39.30	....
Al	6.20	....	6.25

The substance is readily soluble in benzene and carbon disulphide, insoluble in ligroin. It is less stable than the corresponding addition-products with acids and ketones. When heated by itself it begins to decompose below 50°, and the following molecular weight determination shows that it is also partly dissociated in boiling carbon disulphide :

	Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
I.	37.35	1.3160	0.146	570.5
II.	"	2.7290	0.298	594.0
III.	"	4.3430	0.454	606.7
	Calculated for $Al_2Br_6.2(C_6H_5)_2O$,			874.16

The following determination made by the freezing-point method, using benzene as solvent, shows that the substance has the formula given to it:

	Substance. Grams.	Solvent. Grams.	Depression of freezing-point.	Molecular weight.
I.	20.45	0.9215	0.105	854.0
II.	"	2.0480	0.235	840.8
III.	"	2.9910	0.340	860.0
			Mean,	851.6

Calculated for $Al_2Br_6.2(C_6H_5)_2O$, 874.16

2. Phenyl Ether and Aluminium Chloride, $Al_2Cl_6.2(C_6H_5)_2O$. —The substances were brought together in carbon disulphide and the product purified and analyzed like the corresponding compound with aluminium bromide.

The analysis gave the following results:

I. 1.3661 grams substance gave 0.7708 gram $(C_6H_5)_2O$.
II. 0.6421 gram substance gave 0.1085 gram Al_2O_3.
III. 0.1622 gram substance gave 0.2370 gram AgCl.

	Calculated for $Al_2Cl_6.2(C_6H_5)_2O$.	Found. I.	II.	III.
$(C_6H_5)_2O$	56.18	56.43	....	....
Al	8.90	....	8.96	....
Cl	34.91	....	....	34.43

The substance crystallizes in pale-yellow plates, which are very readily soluble in benzene and carbon disulphide.

3. Anisol and Aluminium Bromide, $Al_2Br_6.2(C_6H_5OCH_3)$.—Equivalent quantities of anisol and aluminium chloride were brought together in carbon disulphide solution. The solution was cooled with ice-water and the product precipitated with petroleum ether. Unless the ether is added very slowly to the well-cooled liquid the product separates as an oil.

I. 0.6866 gram substance gave 0.0961 gram Al_2O_3.
II. 0.1841 gram substance gave 0.2745 gram AgBr.

	Calculated for $Al_2Br_6.2C_6H_5OCH_3$.	Found. I.	II.
Al	7.23	7.42	....
Br	63.96	....	63.68

The substance crystallizes in compact, pale-yellow prisms. It is very readily soluble in carbon disulphide, benzene, and anisol. The same product is obtained whether aluminium bromide or anisol is used in excess.

4. Anisol and Aluminium Chloride, $Al_2Cl_6.2C_6H_5OCH_3$.—Freshly distilled aluminium chloride was dissolved in an excess of anisol, the solution diluted with carbon disulphide, and the product precipitated with petroleum ether.

I. 0.7217 gram substance gave 0.1573 gram Al_2O_3.

II. 0.2002 gram substance gave 0.3614 gram AgCl.

	Calculated for $Al_2Cl_6.2C_6H_5OCH_3$.	Found. I.	II.
Al	11.44	11.99	....
Cl	44.97	....	44.46

5. Methylenephenylene Ether and Aluminium Bromide, $Al_2Br_6.2C_{13}H_{10}O$.—A saturated solution of the ether in carbon disulphide was added, drop by drop, to a boiling solution of aluminium bromide in the same solvent. The product separated, on cooling, in the form of fine yellow needles. It was washed with a small quantity of cold carbon disulphide and recrystallized from a mixture of carbon disulphide and low-boiling petroleum ether.

I. 0.8042 gram substance gave 0.3290 gram ether.

II. 0.2654 gram substance gave 0.0293 gram Al_2O_3.

	Calculated for $Al_2Br_6.2C_{13}H_{10}O$.	Found. I.	II.
$C_{13}H_{10}O$	40.54	40.91	....
Al	6.03	....	5.86

The substance is very soluble in carbon disulphide and benzene, almost insoluble in petroleum ether. At 90° to 100° it loses approximately 2 molecules of hydrobromic acid. The residue, on cooling, solidifies to a resinous mass, which could not be obtained in crystalline form. Water decomposes it into methylenephenylene ether and aluminium hydroxide.

II. Compounds with Ketones.

1. Acetophenone and Aluminium Bromide, $Al_2Br_6.2C_6H_5COCH_3$.—Equivalent quantities of the substances were brought together in carbon disulphide and the solution

evaporated in a current of dry air. The product was recrystallized from a mixture of benzene and petroleum ether and dried in a current of air.

I. 0.8204 gram substance gave 0.1099 gram Al_2O_3.
II. 0.2061 gram substance gave 0.4440 gram AgBr.

	Calculated for $Al_2Br_6.2C_6H_5COCH_3$.	Found. I.	II.
Al	7.00	7.12	....
Br	61.97	....	61.50

The substance crystallizes in small colorless plates, which are very slightly soluble in carbon disulphide, more readily in benzene.

2. Acetylmesitylene and Aluminium Bromide, $Al_2Br_6.2C_6H_2(CH_3)_3COCH_3$.—A very dilute solution of acetylmesitylene in carbon disulphide was added to a solution of aluminium bromide in the same solvent and the liquid allowed to stand in a freezing-mixture. In the course of some hours the product separated in the form of large, pale-yellow plates. These were washed with carbon disulphide, dried, and analyzed.

I. 1.1240 grams substance gave 0.4225 gram ketone.
II. 0.8725 gram substance gave 0.1029 gram Al_2O_3.

	Calculated for $Al_2Br_6.2C_6H_2(CH_3)_3COCH_3$.	Found. I.	II.
$C_6H_2(CH_3)_3COCH_3$	37.79	37.59	....
Al	6.31	....	6.26

The substance is very slightly soluble in carbon disulphide and benzene, and has a tendency to separate from solution in the form of an oil which remains liquid for days unless brought in contact with a crystal of the same substance.

3. Diacetylmesitylene and Aluminium Bromide, $Al_2Br_6.C_6H(CH_3)_3(COCH_3)_2$.—The addition-product separates out as a fine powder when a solution of diacetylmesitylene in carbon disulphide is added to a solution of aluminium bromide in the same solvent. The powder was repeatedly washed with boiling carbon disulphide and dried in a current of air.

I. 1.4321 grams substance gave 0.3766 gram ketone.
II. 0.8265 gram substance gave 0.1198 gram Al_2O_3.

	Calculated for $Al_2Br_6.C_6H(CH_3)_3(COCH_3)_2$.	Found. I.	II.
$C_6H(CH_3)_3(COCH_3)_2$	26.65	26.3	....
Al	7.45	....	7.67

The substance was obtained as a fine, reddish-yellow powder, but the color is probably due to some impurity, as the corresponding addition-product with dichloracetylmesitylene is almost colorless. The substance is insoluble in carbon disulphide, slightly soluble in boiling benzene. It dissolves fairly readily in a strong solution of diacetylmesitylene in carbon disulphide and crystallizes out unchanged on cooling. All efforts to get the substance corresponding to the addition-products with monoketones, $Al_2Br_6.2C_6H(CH_3)_3(COCH_3)_2$, failed.

4. Chloracetylmesitylene and Aluminium Bromide, $Al_2Br_6.2C_6H(CH_3)_3COCH_2Cl$. — Chloracetylmesitylene forms only one compound with aluminium bromide. The same substance was obtained in all of the following experiments: (*a*) equivalent quantities of the substances were brought together in carbon disulphide solution; (*b*) a solution of the ketone in carbon disulphide was gradually added to four times the calculated amount of the bromide dissolved in carbon disulphide; (*c*) a solution of the bromide was added to four times the calculated amount of the ketone dissolved in carbon disulphide; (*d*) a solution of the ketone in benzene was added to an excess of the bromide likewise dissolved in benzene; (*e*) the substances were brought together in nitrobenzene and the product precipitated with petroleum ether. The substance crystallizes well and is easily obtained in a pure condition.

I. 1.4114 grams substance gave 0.6012 gram ketone.

II. 0.7757 gram substance gave 0.0876 gram Al_2O_3.

	Calculated for $Al_2Br_6.2C_6H_2(CH_3)_3COCH_2Cl$.	Found. I.	II.
$C_6H_2(CH_3)_3COCH_2Cl$	42.40	42.60	....
Al	5.85	....	5.95

5. Dichloracetylmesitylene and Aluminium Bromide, $Al_2Br_6.C_6H(CH_3)_3(COCH_2Cl)_2$. — A solution of the ketone in carbon disulphide was slowly added to a boiling solution of aluminium bromide in the same solvent. The precipitate was

washed with boiling carbon disulphide and dried in a current of air.

I. 0.9948 gram substance gave 0.3342 gram ketone.
II. 0.8264 gram substance gave 0.1033 gram Al_2O_3.

	Calculated for $Al_2Br_6.C_6H(CH_3)_3(COCH_2Cl)_2$.	Found. I.	II.
$C_6H(CH_3)_3(COCH_2Cl)_2$	33.83	33.56	....
Al	6.72	....	6.63

The substance crystallizes in small, pale-yellow plates. It is sparingly soluble in boiling carbon disulphide and boiling benzene.

6. Dibenzalacetone and Aluminium Bromide, $Al_2Br_6.2(C_6H_5CH:CH)_2CO$.—Equivalent quantities of dibenzalacetone and aluminium bromide were brought together in carbon disulphide solution. The addition-product separated immediately as a red crystalline precipitate.

I. 1.5420 grams substance gave 0.7247 gram ketone.
II. 0.7427 gram substance gave 0.0761 gram Al_2O_3.

	Calculated for $Al_2Br_6.2(C_6H_5CH:CH)_2CO$.	Found. I.	II.
$(C_6H_5CH:CH)_2CO$	46.72	47.00	....
Al	5.41	....	5.56

The substance is only very slightly soluble in carbon disulphide. When prepared as described above, its color is exactly like that of the hydrochloric acid addition-product which is obtained on pouring fuming hydrochloric acid on dibenzalacetone. It dissolves slowly in boiling benzene and crystallizes out again, on cooling, in large, blood-red prisms. In the boiling solution the substance is probably almost completely dissociated, since at this temperature the solution is almost colorless. The color deepens as the temperature falls until, at the ordinary temperature, the color of the solution is the same as that of the addition-product which crystallizes out.

7. Anthraquinone and Aluminium Bromide, Al_2Br_6. $C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_4$.—A solution of anthraquinone in boiling carbon disulphide was added, in small portions, to a boiling

solution of aluminium bromide in the same solvent. The product separated as a fine, brick-red, crystalline powder. This was washed with boiling carbon disulphide, dried, and analyzed.

I. 0.9895 gram substance gave 0.2754 gram anthraquinone.

II. 0.9962 gram substance gave 0.1385 gram Al_2O_3.

	Calculated for $Al_2Br_6.C_{14}H_8O_2$.	Found. I.	II.
$C_{14}H_8O_2$	28.05	27.83	....
Al	7.30	....	7.35

The addition-product is insoluble in carbon disulphide. It dissolves slowly in boiling benzene to form a deep blood-red solution. A similar solution is obtained when aluminium bromide and anthraquinone are brought together in boiling benzene. On cooling the solution, a new substance crystallizes out in blood-red needles. The substance contains 2 molecules of benzene, which it slowly loses at ordinary temperatures, passing back into the brick-red powder described above. To determine the amount of benzene, the substance was heated to 50° in a current of dry air.

I. 1.4250 grams substance lost 0.2422 gram.

II. 1.8261 grams substance lost 0.3126 gram.

III. 1.5135 grams residue, after heating, gave 0.2118 gram Al_2O_3.

	Calculated for $Al_2Br_6.C_6H_4\langle CO \atop CO \rangle C_6H_4.2C_6H_6$.	Found. I.	II.	III.
C_6H_6	17.37	17.00	17.12	....
Al	7.30	....	....	7.76

The substance is extremely unstable. When poured into carbon disulphide or petroleum ether it immediately loses all its benzene, passing into the brick-red compound without going into solution.

8. Xanthone and Aluminium Bromide, $Al_2Br_6.2C_{13}H_8O_2$.—Equivalent quantities of xanthone and aluminium bromide were dissolved in boiling benzene. The product separated, on cooling, in long, yellow needles. After recrystallization from benzene, it was washed with cold carbon disulphide and dried in a current of air.

I. 0.9057 gram substance gave 0.3805 gram xanthone.
II. 0.2195 gram substance gave 0.0250 gram Al_2O_3.

	Calculated for $Al_2Br_6.2C_{13}H_8O_2$.	Found. I.	Found. II.
$C_{13}H_8O_2$	42.33	43.00	....
Al	5.85	....	6.04

The substance is readily soluble in carbon disulphide and benzene.

9. Acetylacetone and Aluminium Bromide.—If a carbon bisulphide solution of aluminium bromide is added to a solution of acetylacetone in ligroin that is kept in a freezing-mixture, a colorless crystalline precipitate separates in fine needles. No hydrobromic acid is evolved during the reaction. It takes 1 molecule of aluminium bromide to precipitate 2 molecules of acetylacetone. If more than this is added the excess is found unchanged in the solution. The precipitate is, therefore, the addition-product $Al_2Br_6.2C_5H_8O_2$. The substance is so exceedingly unstable that it is impossible to dry it without loss of hydrobromic acid. If the temperature is allowed to rise the substance melts and gives off hydrobromic acid. The residue contains 2 atoms of bromine for every atom of aluminium. It is insoluble in carbon disulphide, but dissolves in a solution of acetylacetone containing 2 molecules of the latter for every molecule of aluminium bromide originally used. If this solution is evaporated, hydrobromic acid is given off and the residue contains 1 atom of bromine for 1 atom of aluminium. This residue also dissolves in a carbon disulphide solution of acetylacetone. If the solution is boiled, all the bromine is given off as hydrobromic acid, and pure aluminium acetylacetone crystallizes out when the solution is allowed to cool. Benzoylacetone behaves like acetylacetone, giving pure aluminium benzoylacetone. This is the best way to make aluminium derivatives of these diketones.

III. Compounds with Acid Chlorides.

1. Chloracetyl Chloride and Aluminium Bromide, $Al_2Br_6.2CH_2ClCOCl$.—Aluminium bromide dissolves in chloracetyl chloride. On cooling the solution, an addition-product sepa-

rates in pale-yellow plates. The same substance is formed when chloracetyl chloride is added to an excess of aluminium bromide dissolved in carbon disulphide. The substance was recrystallized from carbon disulphide. It is so exceedingly sensitive to moisture that it is almost impossible to dry it without loss.

I. 0.7227 gram substance gave 0.0990 gram Al_2O_3.
II. 0.1610 gram substance gave 0.2996 gram AgCl(Br).

	Calculated for $Al_2Br_6.2CH_2ClCOCl$.	Found. I.	Found. II.
Al	7.13	7.26	....
Cl } Br }	72.48	....	72.08

2. Terephthalyl Chloride and Aluminium Bromide, $Al_2Br_6.C_6H_4(COCl)_2$.—A solution of terephthalyl chloride in carbon disulphide was slowly added to an excess of aluminium bromide and the liquid boiled for an hour. The addition-product separated as a very finely divided pale-yellow powder. It was repeatedly washed with boiling carbon disulphide, dried, and analyzed.

I. 1.3252 gram substance gave 0.3021 gram terephthalic acid.
II. 0.6536 gram substance gave 0.0915 gram Al_2O_3.
III. 0.3414 gram substance gave 0.6486 gram AgCl(Br).
IV. 0.1821 gram substance gave 0.3480 gram AgCl(Br).

	Calculated for $Al_2Br_6.C_6H_4(COCl)_2$.	Found. I.	Found. II.	Found. III.	Found. IV.
$C_8H_4O_4$	22.55	22.79	....	....	....
Al	7.45	....	7.77	....	....
Cl } Br }	75.60	....	....	73.98	74.44

The substance is insoluble in carbon disulphide. It dissolves in a strong solution of terephthalyl chloride in carbon disulphide, but crystallizes out unchanged, as shown by the analysis (IV.) of a preparation obtained in this way.

3. Terephthalyl Chloride and Aluminium Chloride, $Al_2Cl_6.2C_6H_4(COCl)_2$.—Freshly prepared aluminium chloride was suspended in carbon disulphide and terephthalyl chloride added to the boiling liquid until all the aluminium chloride

dissolved. It took a little more than 2 molecules of terephthalyl chloride to dissolve 1 molecule of the salt. On cooling the solution the addition-product separated in large, transparent plates.

I. 1.2800 grams substance gave 0.6336 gram terephthalic acid.

II. 0.4950 gram substance gave 0.0762 gram Al_2O_3.

	Calculated for $Al_2Cl_6.2C_6H_4(COCl)_2$.	Found. I.	II.
$C_8H_4O_4$	49.90	49.60	....
Al	8.06	....	8.17

Contributions from the Sheffield Laboratory of Yale University.

XCII.—ON THE ACTION OF PHENYLHYDRAZINE ON ACYLTHIOCARBAMIC AND ACYLIMIDOTHIOCARBONIC ESTERS: PYRRO-α,β'-DIAZOLE DERIVATIVES.

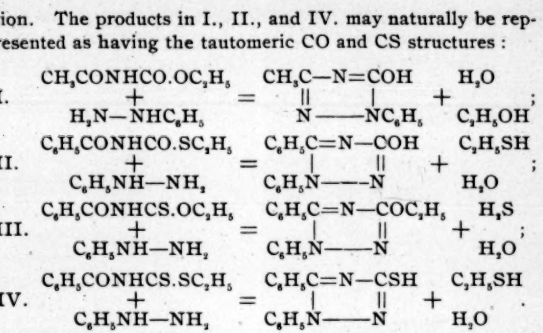
By Henry L. Wheeler and Alling P. Beardsley.

Acetoacetic ester and acetylurethane are attacked by phenylhydrazine in an analogous manner. In both cases the acetyl group, and not the carbethoxy group, is the point of attack by the amino (—NH_2) group of the hydrazine.

The ring-formed compounds that then result are derivatives of 1,3-dialkylpyrazole and 1,3-dialkylpyrrodiazole, respectively.

It might be expected that the thiourethanes—benzoylthiol, thion, and dithiocarbamates—would behave in a similar way. We have found, however, that the urethanes containing sulphur react with phenylhydrazine in precisely the opposite manner; that the —NH_2 group of the hydrazine reacts with the ester group and not with the benzoyl group. Hydrogen sulphide or mercaptan is evolved and 1,5-dialkylpyrrodiazole (triazole) derivatives result instead of the isomeric 1,3 compounds. Examples of the reactions of four types of acylurethanes are tabulated below. They illustrate more definitely the above statements, and they show that four different series of pyrro-α,β'-diazole derivatives result in the reactions in ques-

tion. The products in I., II., and IV. may naturally be represented as having the tautomeric CO and CS structures:



The product in reaction I. was first obtained as above by Andreocci,[1] and the above constitution, *i. e.*, 1-phenyl-3-methyl-5-oxytriazole, was assigned to the compound. This was proved to be correct by Bamberger and de Gruyter,[2] and by Widman.[3]

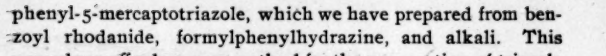
The product obtained by us in reaction II. proved to be identical, in every respect, with the oxytriazole prepared by Young[4] from phenylsemicarbazide, benzaldehyde, and ferric chloride; and by Widman[5] by warming benzoylphenylsemicarbazide with alkali.

The reaction represented by equation III. was investigated by Wheeler and Johnson,[6] in the case of methyl benzoylthioncarbamate, and the product was shown to be 1,5-diphenyl-3-methoxytriazole, by boiling with hydrochloric acid, whereupon the triazole of Young and Widman was obtained.

The proof that the mercaptotriazole formed in reaction IV. is 1,5-diphenyl-3-mercaptotriazole follows from the fact that the same compound results by warming alcoholic solutions of phenylthiosemicarbazide, benzaldehyde, and ferric chloride. This product is entirely different from the isomeric 1,3-di-

[1] Ber. d. chem. Ges., **22**, R. 737 (1889).
[2] *Ibid.*, **26**, 2385.
[3] *Ibid.*, **26**, 2617 (1893).
[4] J. Chem. Soc., **67**, 1063 (1895).
[5] Ber. d. chem. Ges., **29**, 1951 (1896).
[6] This JOURNAL, **24**, 198 (1900).

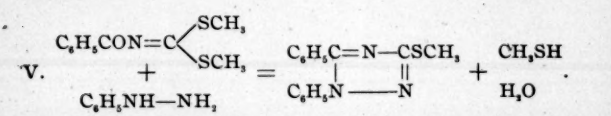
phenyl-5-mercaptotriazole, which we have prepared from benzoyl rhodanide, formylphenylhydrazine, and alkali. This procedure affords a new method for the preparation of triazole derivatives, and the reaction takes place as follows:



In this reaction another compound is formed that is insoluble in alkali. This material agrees in composition with 1,3-diphenyl-2-formyl-5-thiotriazole or 1-phenyl-4-benzoyl-5-thiotriazole or α'-benzoylimido-β'-phenylthiobiazoline. At present, the evidence is in favor of its being regarded as the last-mentioned compound, since on boiling with alkali it decomposes and is not converted into a triazole.

The two products, formed by the action of phenylhydrazine on the benzoyldithiocarbamates on the one hand, and from phenylthiosemicarbazide, benzaldehyde, and ferric chloride on the other, were conclusively shown to be the same by the identity of their alkyl derivatives. These latter, in turn, were identical with the compounds formed by treating the benzoylimidodithiocarbonic esters with phenylhydrazine. Phenylhydrazine therefore acts on the latter series of compounds as follows:

V.



In the case of the above classes of compounds, the tendency of the groups to react with hydrogen of the amino group in phenylhydrazine may be expressed by the following arrangement:

$$CSAlk > CS > CO > COAlk.$$

That is to say, mercaptan is eliminated, rather than hydrogen sulphide, and both these products more readily than water or alcohol, the latter having the least tendency to separate. From this it might be predicted that the acylimidomonothiocarbonic esters would react as follows:

VI. $C_6H_5CON=C(OC_2H_5)SC_2H_5 + C_6H_5NH-NH_2 = C_6H_5C=N-COC_2H_5 \;(C_6H_5N\!-\!N) + C_2H_5SH + H_2O$.

We have found that the reaction takes place as indicated, that mercaptan and water are liberated, and that 1,5-diphenyl-3-ethoxytriazole is formed. In this case it was easy to show that the reaction takes place in two stages. When phenylhydrazine was mixed with benzoylimidothioethyl carbonate in benzene, mercaptan alone was evolved, and the product obtained was benzoylpseudoethylphenylsemicarbazide,

$$C_6H_5CO-NH-C(OC_2H_5)=N-NHC_6H_5.$$

This intermediate product can be crystallized from alcohol and is stable below 136°, at which temperature it loses water and is smoothly converted into 1,5-diphenyl-3-ethoxytriazole.

The stability of this product is especially significant, as it affords an indication of the mechanism of the above reactions. If the acylurethanes are represented as having the pseudo form, $CH_3C(OH)=NCOOC_2H_5$ or $C_6H_5CON=C(OH)SC_2H_5$, etc., then these, as well as the acylimidocarbonic esters, contain a 1,4 double union, $O=C-N=C<$; and phenylhydrazine might be expected to add[1] to these compounds, according to Thiele's theory, in the 1,4 position, as represented by formula VII. This sort of reaction would appear to satisfactorily explain the above triazole formations, were it not for the fact that in the present case it is difficult to reconcile the stability of the intermediate product with this formula.

VII. $C_6H_5C(OH)=N-C(OC_2H_5)(SC_2H_5)-C_6H_5NH-N(H)$

VIII. $C_6H_5CO-NH-C(OC_2H_5)(SC_2H_5)-C_6H_5NH-N(H)$

A compound with an enol structure, such as VII., would separate water and form the triazole more readily than the

[1] That the action of amines on the acylthioncarbamic esters takes place by addition has already been shown in a previous paper. This JOURNAL, 24, 189 (1900).

keto form, VIII., and, therefore, the latter better represents the course of the reaction.

The fact observed by Widman[1] that benzoylphenylsemicarbazide, $C_6H_5CON(C_6H_5)NHCONH_2$, is not transformed into a triazole by heating with acid chlorides, acid anhydrides, or by strongly heating alone, is probably to be explained by the absence of hydrogen adjacent to the benzoyl group. When, however, this compound is treated with alkali it readily gives 1,5-diphenyl-3-oxytriazole. In other words, it appears to us that an unstable alkali addition-product is formed, as has frequently been observed in the case of acid amides, namely,

$$C_6H_5CO(OH.ONa)—NC_6H_5—NHCONH_2,$$

and as this affords the necessary enol condition, the material then readily undergoes condensation.

Now, with this explanation, we were confronted with what at first appeared to be a serious difficulty in accounting for the ease with which the acylthiocarbamates directly form triazoles. For, if the action of phenylhydrazine on benzoyldithiocarbamates, $C_6H_5CONHCS.SR$, results in the formation of a compound analogous to VIII., then by separation of mercaptan, benzoylphenylthiosemicarbazide, $C_6H_5CONH—CS—NH—NHC_6H_5$,[2] must be the intermediate product.

A compound that is represented as having this structure has been prepared by Dixon[3] by combining phenylhydrazine with benzoyl rhodanide. This, however, does not melt even at 220°, while the mercaptotriazole melts at 187° and is easily formed at the temperature of the steam-bath.

In our first experiments we heated the benzoylthiocarbamates with a slight excess of phenylhydrazine, and under these conditions no intermediate product was observed. This suggested the thought that the slight excess of phenylhydrazine employed might have acted by catalysis on the intermediate products, like alkali in the above case. The enol condition thus produced would then readily give rise to condensation. Acting on this supposition, we thereupon carried out the reaction with benzoyldithioethylcarbamate in a cold, dilute, al-

[1] *Loc. cit.* See also Young and Annable: J. Chem. Soc., 71, 204 (1897).

[2] Or a tautomeric form.

[3] J. Chem. Soc. 55, 304 (1889).

coholic solution; mercaptan almost immediately made its presence known, and after standing some time a beautifully crystallized mass of material separated, which proved to be the desired intermediate product.

The curious fact was then observed that this compound melted at 136° and was, therefore, different from the expected benzoylphenylthiosemicarbazide of Dixon. When our material was heated above its melting-point, it gave off water and passed smoothly into 1,5-diphenyl-3-mercaptotriazole, a reaction showing the substance to have the structure which Dixon has assigned to his compound. The explanation of the structure of the latter compound, which now does not immediately concern us, will receive attention at a later time.[1]

The catalytic effect of phenylhydrazine on our benzoylphenylthiosemicarbazide, at the temperature of boiling alcohol, proved to be precisely what was expected. The substance can be repeatedly crystallized from alcohol without alteration. If a couple of drops of phenylhydrazine are added, however, and the boiling continued, the material is quantitatively converted into the mercaptotriazole. The same transformation takes place in the cold with alkali.

The above experiments conclusively show that in these 1,4 unsaturated compounds, a 1,2 and not a 1,4 addition or attack takes place. This is in all probability due to the fact that the form —CONH— is more stable than —COH=N— and that hydrogen has a greater tendency to attach itself to nitrogen than to oxygen.[2]

EXPERIMENTAL PART.

Methyl Benzoylthiolcarbamate, $C_6H_5CONHCOSCH_3$, *and Phenylhydrazine.*—Molecular quantities of the carbamate and phenylhydrazine were mixed in a little alcohol and warmed for several hours on the steam-bath. After the evolution of mercaptan had ceased, the alcohol was evaporated and the residue was treated with warm dilute alkali, whereupon, on

[1] Since the above was written Dr. T. B. Johnson has examined this product and found that it is 1,3-diphenyl-5-mercaptotriazole. See experimental part of this paper.

[2] For other exceptions see Thiele: Ann. Chem. (Liebig), **306**, 105 (1899); **319**, 129 (1901).

acidifying and boiling the precipitate with alcohol, 1,5-diphenyl-3-oxytriazole, melting at 290°, was obtained. A comparison of this material with the product obtained by Young's method[1] showed that the two samples were identical, and when mixed the melting-point was not lowered.

Benzyl Benzoyldithiocarbamate, $C_6H_5CONHCS.SCH_2C_6H_5$, *and Phenylhydrazine.*—The carbamate (30.5 grams) and phenylhydrazine (11.3 grams) were mixed without a solvent, whereupon heat was evolved, and after warming about three hours on the steam-bath the action was complete. The material then crystallized from alcohol in bunches of fine, colorless needles, melting at 187° to 187°.5.

This compound was also obtained from benzoyldithiocarbamic ethylacetate, $C_6H_5CONHCS.SCH_2CO_2C_2H_5$ (5 grams), and phenylhydrazine (1.9 grams). Only a trace of blackening of silver nitrate paper was observed in this preparation (yield of purified material 3.5 grams). Nitrogen determinations gave:

	Calculated for $C_{14}H_{11}N_3S$.	Found. I.	Found. II.
N	16.60	16.38	16.22

It was shown that this product is 1,5-diphenyl-3-mercaptotriazole by preparing it from phenylthiosemicarbazide, benzaldehyde, and ferric chloride. The yield is poor (40 grams of phenylthiosemicarbazide gave about 2.8 grams of the triazole). Prepared in this way it is difficult to purify, and, after repeated crystallizations from alcohol it melted from 0°.5 to 1° too low. When it was mixed with the above material its melting-point was not lowered. The identity of the two products was conclusively shown by the preparation of the ethyl acetate derivatives (see below).

1,5-Diphenyl-3-mercaptotriazole is difficultly soluble in cold alcohol, more readily in hot and in benzene. It is readily soluble in aqueous alkali, and it can be boiled with strong potassium hydroxide with little effect. Its sodium salt is readily soluble in alcohol. In fact, this triazole and its derivatives are characterized by their great stability. It cannot be desulphurized by boiling with freshly precipitated mercuric

[1] *Loc cit.*

oxide. From its solution in ammonia silver nitrate precipitates a bulky, white, amorphous silver salt which is not decomposed by boiling.

An attempt was made to prepare the mercaptotriazole from 1,5-diphenyl-3-chlortriazole,[1] but it was found that this chloride could be fused with potassium hydrosulphide and recovered unaltered.

Ethyl Benzoyldithiocarbamate, $C_6H_5CONHCSSC_2H_5$, *and Phenylhydrazine.*—Seven grams of the former and 3.3 of the latter were mixed in 25 cc. of alcohol and allowed to stand for several hours. Mercaptan made its presence known almost at once, and finally a mass of colorless, six-sided plates or tables separated that had every appearance of being pure. This material melted at 136°–137°, showing signs of melting at 134°, and three crystallizations from alcohol failed to alter the melting-point. On rapidly cooling the alcoholic solutions, the material crystallized in long, slender prisms, which to the naked eye appeared as needles. A nitrogen determination agreed with the calculated for benzoylphenylthiosemicarbazide, $C_6H_5CONHCSNH—NHC_6H_5$:

	Calculated for $C_{14}H_{13}ON_3S$.	Found.
N	15.49	15.65

When this substance was heated above its melting-point it effervesced vigorously at 170° to 180°. On crystallizing then from alcohol it melted at 187° and was found to have been transformed into 1,5-diphenyl-3-mercaptotriazole.

One gram of the material was dissolved in alcohol and 2 or 3 drops of phenylhydrazine were added; on evaporating to dryness and crystallizing from alcohol, in which the material was then much less readily soluble, it was found that the substance had been converted into the above triazole.

A portion was dissolved in cold dilute sodium hydroxide and immediately precipitated by dilute hydrochloric acid, whereupon, without further purification, it melted at 187° to 187°.5.

1,5-Diphenyltriazole-3-monosulphide, $(C_{14}H_{10}N_3)_2S$.—Three grams of the mercaptotriazole and 20 grams of aniline were heated in a closed tube at 270° to 300° for twelve hours. On

[1] Cleve: Ber. d. chem. Ges., **29**, 2672 (1896).

cooling only slight pressure was found in the tube, due to hydrogen sulphide. The contents of the tube were dissolved in alcohol and precipitated with dilute sodium hydroxide. The insoluble part was crystallized from alcohol, whereupon bulky needles of a pinkish-brown shade were obtained which melted at 198°.

This compound was also obtained by heating the mercaptotriazole with paratoluidine at about 180° for thirty hours.

Sulphur determinations gave :

	Calculated for $C_{28}H_{20}N_8S$.	Found. I.	II.
S	6.77	6.96	7.29

1,5-Diphenyltriazole-3-disulphide, $(C_{14}H_{10}N_3)_2S_2$.—The mercaptotriazole was dissolved with one molecular proportion of sodium ethylate in alcohol and somewhat over the calculated quantity of iodine was added. The alcohol was then evaporated and the residue was crystallized from alcohol, whereupon small, colorless pyramids or sharp-pointed crystals, like arrow-heads, were obtained, which melted at 174°. The material was free from iodine, and a nitrogen determination gave :

	Calculated for $C_{28}H_{20}N_8S_2$.	Found.
N	16.66	16.46

1,5-Diphenyl-3-benzoylmercaptotriazole.—Molecular proportions of mercaptotriazole, sodium ethylate, and benzoyl chloride were mixed in alcoholic solution ; the alcohol was then evaporated, the residue washed with water, and crystallized from alcohol, whereupon beautiful, colorless needles, melting at 138°.5, were obtained. A nitrogen determination gave :

	Calculated for $C_{21}H_{15}ON_3S$.	Found.
N	11.78	12.03

1,5-Diphenyl-3-methylmercaptotriazole was prepared from benzoylimidodithiomethyl carbonate and phenylhydrazine (by Dr. T. B. Johnson) and also by methylating the mercaptotriazole by means of sodium ethylate and methyl iodide. In both cases beautiful, colorless tables or six-sided plates, melting at 102° to 103°, were obtained on crystallizing from alcohol.

A nitrogen determination was made from a specimen obtained by the first method.

	Calculated for $C_{15}H_{18}N_3S$.	Found.
N	15.73	15.79

Strong aqueous potash has no effect on this compound. When fused with potassium hydroxide it dissolves, and on acidifying, the mercaptotriazole melting at 187° is obtained.

1,5-Diphenyl-3-ethylmercaptotriazole was obtained by ethylating the mercaptotriazole by means of sodium ethylate and ethyl bromide. On crystallizing from alcohol it forms long, slender, colorless prisms melting at 97°. A nitrogen determination gave:

	Calculated for $C_{16}H_{18}N_3S$.	Found.
N	14.9	15.2

1,5-Diphenyl-3-ethylacetatemercaptotriazole was obtained from the mercaptotriazole prepared from phenylthiosemicarbazide, as well as from that prepared by means of benzyl benzoyldithiocarbamate and phenylhydrazine. In both cases beautiful, colorless prisms were obtained which melted at 67°. When the samples were mixed the melting-point was not lowered. A nitrogen determination gave:

	Calculated for $C_{18}H_{17}O_2N_3S$.	Found.
N	12.39	12.52

1,5-Diphenyl-3-benzylmercaptotriazole.—This was obtained in three ways. It was first prepared by warming molecular quantities of benzoylimidodithiobenzylcarbonic ester and phenylhydrazine on the steam-bath. The mercaptan evolved was removed by distilling under diminished pressure and the residue was crystallized from alcohol, whereupon beautiful, flattened, colorless prisms, clustered in the form of balls, were obtained. These melted at 100° to 100°.5, and a nitrogen determination was made with the result given below.

This compound was also obtained by treating the mercaptotriazole with alkali and benzyl chloride.

	Calculated for $C_{21}H_{17}N_3S$.	Found.
N	12.24	12.27

It was found that this compound was the chief product when phenylhydrazine was allowed to act on the following ester :

Di(benzoylimidodithiobenzyl)ethylene Ester, $C_6H_5CON=C(SCH_2C_6H_5)SCH_2CH_2S(C_6H_5CH_2S)C=NCOC_6H_5$. — This was prepared from benzoyldithiobenzyl carbamate by means of sodium ethylate and ethylene bromide in alcoholic solution. It crystallizes from alcohol in the form of fine, colorless, radiating needles, having a faint green tinge, and it melts at 93°.5 to 94°. A nitrogen determination gave :

	Calculated for $C_{32}H_{28}O_2N_2S_4$.	Found.
N	4.66	4.84

The Ethylacetate Derivative of Acetyldithiocarbamic Acid, $CH_3CONHCSSCH_2CO_2C_2H_5$.—This was made by warming thiocyanethylacetate with thioacetic acid. It formed yellow needles or slender prisms from a mixture of benzene and petroleum ether, which melted at 82°, and a nitrogen determination gave :

	Calculated for $C_7H_{11}O_2NS_2$.	Found.
N	6.33	6.51

When 2.7 grams of this were mixed with 1.5 grams of phenylhydrazine, in some alcohol, and warmed for several hours on the steam-bath, a product was obtained which crystallized from alcohol in colorless prisms and was difficultly soluble. It melted at 163° to 164° and a nitrogen determination agreed with the calculated for *1-phenyl-5-methyl-3-mercaptotriazole :*

	Calculated for $C_9H_9N_3S$.	Found.
N	21.9	21.7

1-Paratolyl-5-phenyl-3-mercaptotriazole, from normal propylbenzoyldithiocarbamate and paratolylhydrazine, formed colorless needles or prisms, from alcohol, which melted at 170° to 171°, showing signs of melting at 168°. A nitrogen determination gave :

	Calculated for $C_{15}H_{13}N_3S$.	Found.
N	15.73	16.00

Benzoylimidomonothioethylcarbonate, $C_6H_5CON=C\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix}$, *and Phenylhydrazine.*—When molecular quantities of the above substances were dissolved in benzene the odor of mercaptan was soon noticed, and on standing several hours a mass of crystals separated. On crystallizing these from alcohol, radiating groups of fine needles were obtained which melted at 136°, with effervescence due to the escape of water. A nitrogen determination agreed with the calculated for benzoylpseudoethylphenylsemicarbazide, $C_6H_5CONHC(OC_2H_5)=N—NHC_6H_5$:

	Calculated for $C_{18}H_{21}O_2N_3$.	Found.
N	14.8	15.1

When the calculated quantities of the above carbonate and phenylhydrazine were mixed and heated in a bath at 140°, mercaptan and water were evolved, and on crystallizing the residue from dilute alcohol, fine needles were obtained which melted at 90°. Young[1] gives the melting-point of 1,5-diphenyl-3-ethoxytriazole as 92°. We therefore prepared this substance by his method and found that it also melts at 90°, and that on mixing the two products no reduction in melting-point took place.

One gram of the pseudosemicarbazide was dissolved in alcohol and 3 drops of phenylhydrazine were added. The mixture was evaporated on the steam-bath, and, after about an hour, crystallized from alcohol, whereupon it was found that the material had been converted into the ethoxytriazole which melts at 90°.

1,3-Diphenyl-5-mercaptotriazole.—This mercaptotriazole, isomeric with the one obtained from the benzoyldithiocarbamates and phenylhydrazine, was prepared as follows: Five grams of formylphenylhydrazine and 6 of benzoylrhodanide were mixed and heated sufficiently to melt the mixture. The material was then allowed to remain on the steam-bath for a number of hours. It was then treated with cold dilute sodium hydroxide, filtered from insoluble material, and the triazole

[1] *Loc. cit.*

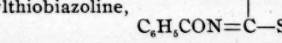
precipitated by dilute hydrochloric acid. The precipitate, on crystallizing from alcohol, formed pure white, hair-like bunches of needles, which sinter and then melt at about 248° to 249°. The following results were obtained on analysis:

	Calculated for $C_{14}H_{11}N_3S$.	Found.
N	16.60	16.38
S	12.65	12.85

The material insoluble in alkali was crystallized from alcohol, whereupon long needles or thin prisms were obtained which melted at 119° to 120°. This formed the larger part of the above reaction-product. The analytical results agreed with the calculated for a condensation of equal molecules of benzoyl rhodanide and formylphenylhydrazine minus water.

	Calculated for $C_{18}H_{11}ON_3S$.	Found.
N	14.9	15.1
S	11.39	10.79

A portion of the material was boiled with dilute alkali; nearly all dissolved and an odor of aniline or phenylhydrazine was noticed. On adding dilute hydrochloric acid, benzoic acid was precipitated. Benzoic acid was also obtained on warming with dilute hydrochloric acid. These experiments show that the material is easily decomposed. From this it is improbable that the compound is a triazole, and, therefore, at present we are inclined to the view that it is α'-benzoylimido-β'-phenylthiobiazoline,



αα-Carbethoxyphenylsemicarbazide, $C_2H_5OCO(C_6H_5)N—NHCONH_2$, was prepared from phenylsemicarbazide and an excess of chlorcarbonic ester by warming on the water-bath. It was crystallized from a mixture of alcohol and benzene (2 volumes of alcohol and 3 volumes of benzene). Rapid crystallization produced bunches of very fine, hair-like needles, while slow gave compact bunches of small prisms. It melts at 171.5°, and a nitrogen determination gave:

	Calculated for $C_{10}H_{13}O_3N_3$.	Found.
N	18.83	18.78

This substance is difficultly soluble in benzene, quite soluble in alcohol, and it may be crystallized from water. With sodium hydroxide, sodium ethylate, and acetyl chloride, phenylurazole melting at 263° is formed. Boiling chlorcarbonic ester has no effect on the compound, while if it is melted it decomposes. When warmed with phenylhydrazine, on the water-bath, it remained unaltered.[1]

NEW HAVEN, CONN., Feb. 6, 1902.

XCIII.—ON THE MOLECULAR REARRANGEMENT OF UNSYMMETRICAL ACYLTHIOUREAS AND ACYLPSEUDOTHIOUREAS TO ISOMERIC SYMMETRICAL DERIVATIVES.

BY HENRY L. WHEELER.

The interesting observation was made by Hugershoff[2] that by the action of acetic anhydride on monophenylthiourea an unstable acetylphenylthiourea first results, which melts at 139°. On heating this substance above its melting-point a molecular rearrangement takes place, and the material is transformed into an isomeric acetylphenylthiourea melting at 171°. The latter is identical with the product obtained from acetylisothiocyanate and aniline.[3] These isomers are sharply distinguished by their properties, and especially by their behavior with mercuric oxide and with alkali. Hugershoff found that the labile acetyl derivative, melting at 139°, is readily desulphurized by mercuric oxide, yielding acetylphenylurea, while the stable derivative, obtained by heating

[1] In the February number of this JOURNAL, Acree describes this compound as dicarbethoxyphenylsemicarbazide and two carbon and hydrogen determinations are given in support of his view. The amount of carbon for a mono- and dicarbethoxy derivative differs by only 0.98 per cent., while that of hydrogen is the same. On the other hand, that of nitrogen differs by 4.60 per cent. We, therefore, prepared the compound by Acree's directions and observed that the material melted at 171.5° and when mixed with ours the melting-point was not altered. A nitrogen determination gave:

	Calculated for $C_{12}H_{17}O_5N_3$.	Calculated for $C_{10}H_{13}O_3N_3$.	Found.
N	14.23	18.83	19.20

The compound is therefore a monocarbethoxy derivative. Acree states that on crystallizing his material from water the melting-point is lowered. Our material was found to behave in the same manner.

[2] Ber. d. chem. Ges., **32**, 3649 (1899).

[3] Miquel: Bull. Soc. Chim., [1], **28**, 252.

the labile one, is unaffected by mercuric oxide. He concludes, from the analogous behavior of diphenylthiourea, that this action of mercuric oxide alone is sufficient to show that the labile acetyl derivative has the following structure:

$$C_6H_5NHCSNHCOCH_3.$$

For the stable derivative the isomeric pseudo or tautomeric form, $C_6H_5N{=}C(SH)NHCOCH_3$, is assumed. The existence of these isomers is, according to this, merely a case of desmotropism.

Both the labile and stable derivatives dissolve in alkali of a dilution of 15 : 1000. On subsequently precipitating with carbon dioxide or hydrochloric acid, only the stable form is obtained. With strong alkali, 15 : 100, the labile does not dissolve, but a mass of crystals of acetanilide and phenylthiourea almost immediately form, while in solution are the sodium salts of thiocyanic and acetic acids. The stable urea, on the other hand, dissolves in strong alkali and can be reprecipitated unaltered.

Besides monophenylthiourea, several other monoarylthioureas were found to give isomeric acetyl derivatives,[1] but disubstituted ureas, diphenylthiourea, etc., gave only one acetyl compound.

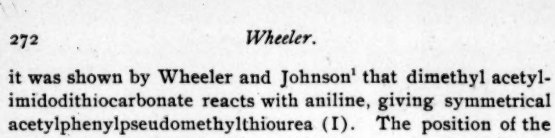
In regard to other explanations of the existence of these isomers, the possibility that they are stereochemical modifications was considered, only to be rejected on account of the behavior of the labile ureas toward mercuric oxide.

The idea that the labile acetyl derivatives are unsymmetrical acetylarylureas, $CH_3CO(C_6H_5)N{-}CS{-}NH_2$, is not mentioned by Hugershoff, although the lack of corresponding isomers in the case of disubstituted ureas is especially significant, and moreover, the behavior of the labile compounds with strong alkali will scarcely permit of any other explanation.

The writer proposes to show now that these labile ureas belong to the hitherto unknown or unrecognized class of unsymmetrical acylthioureas, and that the isomerism in question does not depend on the existence of both a normal and a pseudo form. This is proved as follows: In a previous paper

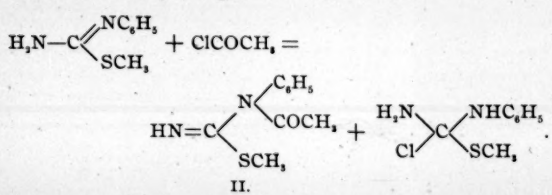
[1] Hugershoff and König: Ber. d. chem. Ges., **33**, 3029 (1900).

it was shown by Wheeler and Johnson[1] that dimethyl acetylimidodithiocarbonate reacts with aniline, giving symmetrical acetylphenylpseudomethylthiourea (I). The position of the acetyl group in the resulting acylpseudourea is shown by its method of formation:



I.

Now by careful treatment of phenylpseudomethylthiourea, $H_2N—C(SCH_3)=NC_6H_5$, with acetyl chloride a product can be obtained isomeric with the above acetylphenylpseudomethylthiourea. Since only two structurally different acetyl derivatives are possible, this reaction must take place as follows: The acetyl chloride unites with the tertiary phenylimido group and then separates hydrogen chloride, giving unsymmetrical acetylphenylpseudomethylthiourea (II), and the hydrochloride of phenylpseudomethylthiourea:[2]

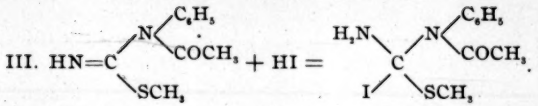


II.

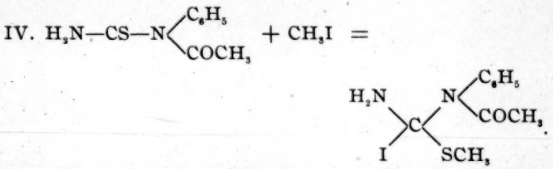
This unsymmetrical acetyl derivative has basic properties, since, on treating in ether with dry hydrogen iodide, it gives an immediate precipitate of a hydroiodide or addition-product, which can be repeatedly crystallized from alcohol. This melts at 152°.

[1] This JOURNAL, **26**, 412 (1901).

[2] The Schotten-Baumann method has been used with success for the preparation of the corresponding unsymmetrical benzoyloxygenpseudoureas by Stieglitz and McKee: This JOURNAL, **26**, 230 (1901). In the present case, owing to the unstable nature of the products, this method could not be employed.

III. 

Finally, Hugerhoff's labile urea, on standing a few hours with methyl iodide, gives a methyl iodide addition-product that is identical in melting-point, in properties, and in fact in every respect, with the above hydroiodide. The addition in this case therefore takes place as follows :

IV. 

On the other hand, the hydrogen iodide addition-product obtained from symmetrical acetylphenylpseudomethylthiourea melts at about 116°, and it has entirely different properties from those of the product obtained by methods III. and IV. The following, therefore, represents the formation and structure of this salt :

V.

The fact that these two salts are different shows that a molecular rearrangement does not take place in their preparation, and it excludes the possibility that the labile and stable forms are stereochemical isomers. Were this latter assumption true, one and the same hydroiodide would be formed by all three methods.

The identity of the products formed by adding hydrogen iodide to our unsymmetrical acetylphenylpseudomethylthiourea, on the one hand, and methyl iodide to Hugerhoff's

labile derivative on the other, therefore proves that the series of labile thioureas have the aryl and acetyl groups attached to the same nitrogen atom. It follows from this that the molecular rearrangement which takes place when these labile ureas are heated is as follows:

VI. $H_2N—CS—N(C_6H_5)COCH_3 \rightarrow CH_3CONH—CSN(C_6H_5)H$,

or VII. $HN=C(SH)N(C_6H_5)COCH_3 \rightarrow CH_3CONH—C(SH)=NC_6H_5$.

According to VI. the acetyl group and hydrogen simply change place; or, if the acetylthioureas have the pseudo form, the rearrangement may involve a migration of the acetyl group and shifting of the double bond, as shown in formula VII. At any rate, unsymmetrical acetylthioureas are transformed into symmetrical isomers on heating.

This interesting molecular rearrangement is not confined to the acylthiourea series. Dr. Treat B. Johnson and I have found that the same behavior is met with in the case of unsymmetrical acetyl- and benzoylpseudothioureas. For example, the above unsymmetrical acetylphenylpseudomethylthiourea, II., simply on melting, is transformed into the stable symmetrical acetylphenylpseudomethylthiourea, I. It follows from this that the sulphur atom takes no part in these rearrangements.[1]

The melting-points of the isomeric acetylphenylpseudomethylthioureas differ by only 2°, and curiously, the stable form has the lower melting-point, *viz.*, 82° to 83°. However,

[1] These cases, therefore, present examples of unsymmetrical amidines undergoing a metastatic change into symmetrical amidines, and the author believes we can draw the conclusion that when but one form of a "tautomeric" substance is known, it corresponds to the stable form which is produced by heating the labile acyl or alkyl derivative. The normal alkylthiocyanates undergo a molecular rearrangement into isothiocyanates, $NCSR \rightarrow RNCS$; therefore thiocyanic acid has the structure HNCS. The imidoesters are transformed into alkyl amides; the amides are derivatives of the keto form, $OC(—N<)$ (Wislicenus and Goldschmidt: Ber. d. chem. Ges., 33, 1470). Since the isonitriles are converted into nitriles by simple molecular rearrangement, hydrogen cyanide should have the structure HCN. In the transformation of the substituted amidines or acylpseudothioureas the stable form is shown to be $H_2N—C(R)=NC_6H_5$, and, therefore, the question of the structure of monophenylbenzenyl and similar amidines should be decided in favor of the above, instead of the form $HN=C(R)—NHC_6H_5$ (Peckmann: Ber. d. chem. Ges., 30, 1781 (:897)). This view will receive further attention at a later time.

in the case of unsymmetrical benzoylpseudomethylthiourea and unsymmetrical benzoylphenylpseudobenzylthiourea, the melting-points of the isomers are widely different, and the change on heating is most striking. When the first-mentioned benzoyl derivative is heated it melts at 86° to 87°, sharply and completely. If cooled and reheated, it no longer shows the slightest trace of melting at 86° to 87°, the heating having transformed the material into the stable symmetrical derivative, which melts at 104°. The latter compound was prepared by Wheeler and Merriam[1] from dimethyl benzoylimidodithiocarbonate and aniline.

This molecular rearrangement takes place even more readily than that of Hugerhoff's labile compounds, inasmuch as our labile derivatives cannot be crystallized from alcohol. In fact, even on standing in cold alcohol they pass into the stable isomers as follows :

$$HN{=}C(SCH_3)N(C_6H_5)COC_6H_5 \rightarrow C_6H_5CONH{-}C(SCH_3){=}NC_6H_5 \quad \text{VIII.}$$

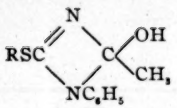
The behavior of the labile and stable acylphenylpseudothioureas with alkali is perfectly analogous to that of the corresponding acetylphenylthioureas. Labile acetylphenylpseudomethylthiourea gives acetanilide and methyl thiocyanate, the decomposition taking place as follows :

$$HN{=}C(SCH_3)NC_6H_4COCH_3 = NCSCH_3 + HNC_6H_4COCH_3.$$

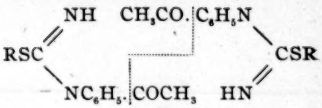
On the other hand, alkali merely dissolves the stable products, leaving no insoluble material, and no anilides are formed. On adding acid, unaltered material is precipitated. An excess of hydrochloric acid, however, redissolves the precipitates. They are, therefore, best precipitated by carbon dioxide.

The study of the molecular rearrangement described in this paper will be continued, in order to determine whether the reaction is monomolecular, involving an inner condensation according to IX., or dimolecular with the character of a saponification, X. :

[1] J. Am. Chem. Soc., **23**, 293 (1901).



IX.



X.

We also wish to determine whether or not this molecular rearrangement can be accomplished in the case of other unsymmetrical thiourea derivatives, with radicals other than the acyl group, and we ask that this work be left to us.

EXPERIMENTAL PART.

Unsymmetrical Acetylphenylpseudomethylthiourea, $CH_3CO(C_6H_5)N{-}C(SCH_3){=}NH$.—This was prepared by dissolving 15 grams of phenylpseudomethylthiourea[1] in a little over 150 cc. of pure dry ether, and then slowly dropping in 3.5 grams of acetyl chloride in 30 cc. of ether. During the operation the whole was cooled in a freezing-mixture. Phenylpseudomethylthiourea hydrochloride separated as a white mass, and the reaction was complete as soon as the acetyl chloride was all added. On filtering then and evaporating the ether spontaneously, beautiful, colorless prisms separated. These were about the size of grains of rice. The melting-point was found to be 85° to 86°, and a nitrogen determination gave :

	Calculated for $C_{10}H_{12}ON_2S$.	Found.
N	13.46	13.51

Behavior with Alkali.—When this material was stirred with cold dilute alkali it immediately decomposed, becoming oily, and the odor of methyl thiocyanate was noticed. On filtering and crystallizing the insoluble material from water, plates of pure acetanilide, melting sharply at 114°, were obtained. When this was mixed with acetanilide the melting-point was not changed. Carbon dioxide, when passed into the alkaline filtrate, produced no precipitate (absence of isomer).

Behavior on Heating.—Some of the material was warmed on the steam-bath for several hours. It was then treated with alkali, when nearly all dissolved, and, on passing carbon di-

[1] Bertram : Ber. d. chem. Ges., **25**, 49 (1892).

oxide into the alkaline solution, a mass of colorless, needle-like prisms separated, which proved to be symmetrical acetylphenylpseudomethylthiourea,

$$CH_3CONH—C(SCH_3)=NC_6H_5,$$

melting at 82° to 83°.[1]

Behavior with Hydrogen Iodide.—Dry hydrogen iodide passed into the ethereal solution gave an immediate precipitate. This was difficultly soluble in cold alcohol, but readily in hot; it separated, on cooling, in the form of colorless, four- and six-sided tables and prisms, and it melted at 152° with strong effervescence, forming a clear, red liquid. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}ON_2SI$.	Found.
N	8.33	8.48

This material is, therefore, unsymmetrical acetylphenylpseudomethylthiourea hydroiodide,

$$CH_3CO(C_6H_5)N—C(SCH_3)INH_2.$$

Unsymmetrical Acetylphenylthiourea and Methyl Iodide.—Hugerhoff's labile acetyl derivative melting at 139° was prepared according to his directions. It was finely pulverized and then suspended in a large excess of methyl iodide and allowed to stand for twenty-four hours; the material did not dissolve, but, nevertheless, the reaction was complete at the end of the above time. On crystallizing from alcohol it formed the same characteristic tables as the above hydroiodide, and melted sharply at 152°, with effervescence, to a red liquid. When mixed with the above hydrogen iodide addition-product, the melting-point or temperature at which effervescence began was not altered.

Both these products, moreover, showed the same behavior with aqueous alkali. In the cold the material is immediately decomposed, acetanilide and methylthiocyanate being formed. There can, therefore, be no doubt that the compounds are identical. A nitrogen determination gave:

[1] Wheeler and Johnson: This JOURNAL, **26**, 412 (1901).

	Calculated for $C_{10}H_{19}ON_2SI$.	Found.
N	8.33	8.64

Symmetrical Acetylphenylpseudomethylthiourea and Hydrogen Iodide.—The symmetrical pseudothiourea was prepared from dimethyl acetylimidodithiocarbonate. In regard to the preparation of this it was stated[1] in our article that only one-half of the reaction-product of dimethyl acetyldithiocarbamate, sodium ethylate, and methyl iodide consisted of the ester. This was due to the fact that the action was carried out at ordinary temperature. If conducted, however, at a temperature near 0° the entire product, almost from the first to the last drop, boils at 148° at 24 mm. pressure. This material was mixed with aniline in a little alcohol, whereupon, on standing, symmetrical acetylphenylpseudomethylthiourea melting at 82° to 83° was obtained. This was dissolved in ether, and hydrogen iodide gave a bulky precipitate, which was thoroughly washed with anhydrous ether. It melted at about 116°, with effervescence. On attempting to crystallize from alcohol it was found that the material was much more soluble than the isomeric hydroiodide, and on boiling the alcoholic solution the salt was decomposed. It could be precipitated from its alcoholic solution by ether. A nitrogen determination gave :

	Calculated for $C_{10}H_{19}ON_2SI$.	Found.
N	8.33	8.41

The behavior of this salt with alkali served to distinguish it sharply from the isomer. In dilute alkali it immediately dissolved to a clear solution, and on passing in carbon dioxide, a well crystallized mass of needle-like prisms separated, which melted sharply at 82° to 83° (symmetrical acetylphenylpseudomethylthiourea).

Symmetrical acetylphenylthiourea and methyl iodide did not react under the same conditions as the unsymmetrical derivative.

Unsymmetrical Benzoylphenylpseudomethylthiourea. — Ten grams of phenylpseudomethylthiourea were dissolved in 100

[1] Wheeler and Johnson : This JOURNAL, **26**, 192 (1901).

cc. of dry ether and to the cooled solution 4.2 grams of benzoyl chloride, in 40 cc. of ether, were slowly added. On filtering and evaporating spontaneously, a snow-white mass of needles separated, which melted at 86°. A nitrogen determination gave :

	Calculated for $C_{16}H_{14}ON_2S$.	Found.
N	10.37	10.59

The behavior with alkali is perfectly analogous to that of the labile acetyl derivative. The material, without dissolving, is converted into benzanilide and methyl thiocyanate.

Behavior on Heating.—The material melted sharply and completely at 86°, but on cooling and reheating there was no sign of melting below 90° ; then up to 104° the substance melted. It was found that this labile compound could not be crystallized unchanged from alcohol. If the solution was boiled and then cooled, large, thin, colorless plates were obtained, which melted sharply at 104°, the melting-point of symmetrical benzoylphenylpseudomethylthiourea.[1]

In fact, on simply standing in cold alcohol the material undergoes this molecular rearrangement. If rapidly evaporated by means of a current of air, the alcoholic solution deposits needles of unaltered labile material, less rapid evaporation gives needles or thin prisms, and some tables, slow evaporation produces large tables, the tables being the rearranged product.

Symmetrical benzoylphenylpseudomethylthiourea, which crystallizes either in large, thin plates or tables, and melts at 104°, is readily soluble in alkali ; from this solution carbon dioxide precipitates the unaltered material in crystalline form.

Unsymmetrical Benzoylphenylpseudobenzylthiourea, $C_6H_5CO(C_6H_5)N—C(SCH_2C_6H_5)=NH$, by Dr. Treat B. Johnson.—In our article on acetyl and benzoylpseudothioureas[2] we described the stable form of this urea. We found that, by treating phenylpseudobenzylthiourea[3] with benzoic anhydride and crystallizing the product from alcohol, symmetrical ben-

[1] Wheeler and Merriam : J. Am. Chem. Soc., **28**, 293 (1901).
[2] *Loc. cit.*
[3] This JOURNAL, **26**, 419 (1901).

zoylphenylpseudobenzylthiourea, melting at 116° to 117°, was obtained. An entirely different result was brought about when the pseudourea was treated with benzoyl chloride in ether, and the ether allowed to evaporate spontaneously. The material thus obtained, on washing with cold alcohol, melted at 92° to 92°.5. A nitrogen determination gave :

	Calculated for $C_{21}H_{18}ON_2S$.	Found.
N	8.09	8.10

When this was treated with alkali, benzanilide and benzyl thiocyanate were obtained.

When heated or crystallized from boiling alcohol, the material was transformed into symmetrical benzoylphenylpseudobenzylthiourea, which dissolved unaltered in alkali and was precipitated by carefully adding hydrochloric acid. The stable urea dissolves in an excess of hydrochloric acid. The statement, previously made by us, that the acylpseudothioureas appear to have no basic properties was founded on the fact that their benzene solutions gave no precipitate with hydrogen chloride. The salts which are formed under these conditions are soluble in benzene.

NEW HAVEN, CONN., February, 1902.

XCIV.—ON SOME DOUBLE SULPHATES OF THALLIC THALLIUM AND CAESIUM.

BY JAMES LOCKE.

Among the most characteristic compounds formed by members of the first sub-group in the third family in the periodic system are the alums. All three of the lighter elements of the group, aluminium, gallium, and indium, yield them ; and in strict analogy to its prototypes, therefore, thallic thallium should form salts of the same nature. The general impression does seem to exist, in fact, that thallic alums have been prepared ; partly owing, perhaps, to the general tendency of chemists to assume, off-hand, a strong analogy between all the members of a family, and partly to a paper by Lepsius.[1] This investigator obtained a double sulphate of thallous and

[1] Verh. Naturforsch. u. Aerzte, **63**, [2] 103 ; Centrbl., 1891, I., 694.

thallic thallium, of the formula $Tl^{I}Tl^{III}(SO_4)_2$, which, he says, "is to be regarded as an anhydrous alum....., etc.," and this expression has crept into the handbooks.

There is certainly no more reason why an anhydrous double sulphate of thallium should be regarded as an alum than should a similar salt of cerium, or iridium, or any other trivalent metal. That it is so called is a very good instance of the arbitrary manner in which analogy is often found in the system when it happens to be more needed than self-evident. The double sulphates of thallic thallium with sodium and potassium are likewise anhydrous, and so far as is known, therefore, absolutely no indication of power on the part of thallic sulphate to form alums has been observed.

In view of the position of the element in the system, however, such compounds would, of course, attain considerable importance, and at my suggestion, therefore, Mr. David E. Breinig has undertaken to ascertain whether, under perhaps more favorable conditions, one could not be prepared. It has been shown by Piccini[1] that caesium yields alums far more readily than do any of the other univalent metals. My own experience, also, has shown, that while the sulphates of some of the trivalent metals, *e. g.*, iron, indium, etc., unite with most of the alkali sulphates to form salts containing less than 12 molecules of water, often more readily, in fact, than they form the alums, not one of the alum-forming trivalent metals yields with caesium more than the one hydrated salt.[2]

The failure of the sulphate of a given trivalent metal to unite with caesium sulphate to a compound of the type $CsM^{III}(SO_4)_2.12H_2O$ may therefore be taken as an almost positive indication that such element has no alum-forming power whatsoever. This we have found to be the case with thallic thallium. Its sulphate was crystallized with caesium sulphate under the most varied conditions, from both hot and cold solutions, and under no circumstances could the formation of the isometric crystals of an alum be observed. Two different hydrated double salts were obtained, and possibly a third. But they all contained much less water than is called

[1] Ztschr. anorg. Chem., **17**, 355, etc.
[2] This JOURNAL, **26**, 166.

for by a compound of the alum series. Although as far as its main purpose is concerned, therefore, the results of our investigation were entirely negative, except in that they establish the strong improbability that thallic alums are capable of existence, if it may be well to describe the salts obtained during our experiments, as a slight contribution to the literature of the thallic compounds in general.

The thallic sulphate used was prepared by treating the freshly precipitated hydroxide with the calculated quantity of concentrated sulphuric acid and adding first the desired quantity of water, and then enough more sulphuric acid to bring the salt into clear solution. To this the requisite amount of a concentrated solution of caesium sulphate was added. On mixing even a small proportion of the latter with a fairly concentrated cold solution of the thallic sulphate, a compact white precipitate at once separates out, which is very sparingly soluble in cold water, but dissolves readily upon application of heat. Recrystallization of a product obtained with equivalent quantities of caesium sulphate and thallium sulphate yielded small, well-formed, prismatic crystals, which probably belong to the rhombic system. Seen under the microscope they were almost colorless and of a characteristic hemimorphous habit. The same crystals were obtained with varying quantities of caesium sulphate, at all temperatures from 40° to 0°. The products were in all cases perfectly homogeneous, no isometric crystals at all being observed. A quantity of this salt was recrystallized from sulphuric acid solution, and after washing with more dilute acid and drying as perfectly as possible, was submitted to analysis. The various constituents were determined in separate portions. The thallium was weighed as iodide and the caesium as sulphate, after removal of the thallium by means of ammonium sulphide. The water was estimated directly, by ignition in a tube containing lead oxide. The results correspond fairly well with the formula

$$CsTl(SO_4)_2.3H_2O:$$

The somewhat high percentage of sulphuric acid found is due to the difficulty of removing the latter from the recrystallized

salt. The latter is at once decomposed by water or 95 per cent alcohol, and a considerable quantity of sulphuric acid must be present in the wash-water to prevent hydrolysis:

	Calculated for $CsTl(SO_4)_2.3H_2O$.	Found.
Cs	22.81	21.80
Tl	34.98	34.40
SO_4	32.95	34.21
H_2O	9.26	8.62
	100.00	99.03

A second salt was obtained from the mother-liquor of the above by evaporating to a high point of concentration of the sulphuric acid and allowing to cool. This body separates in the form of thin, highly lustrous plates, which, under the microscope, proved to consist of very regularly-formed rhombic plates. The crystals are so transparent that in clusters of 5 or 6 superimposed plates the edges of the undermost can readily be seen through the others. It was impossible to obtain a completely satisfactory analysis of this salt, owing to its hygroscopic nature and the difficulty of removing the concentrated acid. One product was obtained with 5.21 per cent water, and the caesium and thallium were in the ratio 1 : 1. Its composition, according to these data, would be

$$CsTl(SO_4)_2.1\tfrac{1}{2}H_2O.$$

For this formula 4.86 per cent H_2O is required.

Incidentally to the above experiments, attempts were made to prepare an alum with chromic acid instead of sulphuric. With one exception, the observed analogy between chromates and sulphates has hitherto been confined purely to simple salts, this instance being found in the compound

$$(NH_4)_2Mg(CrO_4)_2.6H_2O,$$

which is isomorphous with the corresponding double sulphates.

The most sparingly soluble alums being those of aluminium, solutions of aluminium chromate and caesium dichromate were crystallized together in all proportions and at various temperatures. Under no conditions

could the formation of an alum be observed. Sulphuric acid was then added, in the hope that mixed chromate and sulphate alum crystals might be obtained, this having been shown by Retgers[1] to be a most delicate test for the isomorphism of two compounds, one of which is colored. The small octahedrons of caesium aluminium alum which were deposited, however, proved to be perfectly colorless, and entirely free from chromium. It would seem, therefore, that, at least within ordinary limits of temperature, chromic acid, as well as thallic thallium, has no tendency at all to enter into alums.

NEW HAVEN, CONN., February, 1902.

THE SULPHATES OF BISMUTH.

BY. F. B. ALLAN.

An acid sulphate of bismuth, $Bi_2O_3.4SO_3$, with 1, 3, 7, or $10H_2O$, has recently been described by Adie.[2] He obtained it by crystallization from sulphuric acid of greater concentration than $H_2SO_4.5H_2O$ (=52 per cent H_2SO_4), the amount of water in the salt depending on the concentration of the acid and on the temperature. It has also been described by Leist.[3]

$Bi_2O_3.3SO_3$ has been obtained by heating the acid sulphate (Schultz-Sellac,[4] Hensgen[5]). Only double salts containing it have been obtained in the wet way.

$5Bi_2O_3.11SO_3.17H_2O$ crystallizes from sulphuric acid of concentration $H_2SO_4.6H_2O$ (=47.5 per cent) to $H_2SO_4.12H_2O$ (=31 per cent) [Adie].

$Bi_2O_3.2SO_3.2H_2O$ and $Bi_2O_3.2SO_3.3H_2O$ crystallize from dilute sulphuric acid (Leist, Heintz,[6] Luddecke,[7] Ruge[8]).

$Bi_2O_3.SO_3$ is formed by the action of water on $Bi_2O_3.2SO_3$ (Heintz, Ruge, Hensgen).

[1] Ztschr. phys. Chem., **3**, 497.
[2] Proc. Chem. Soc., 1899, p. 226.
[3] Ann. Chem. (Liebig), **160**, 29.
[4] Ber. d. chem. Ges., **4**, 13.
[5] Rec. trav. chim. Pays-Bas., **4**, 399.
[6] Pogg. Ann., **63**, 55.
[7] Ann. Chem. (Liebig), **140**, 277.
[8] J. prakt. Chem., **96**, 138.

$4Bi_2O_3.3SO_3.15H_2O$ was prepared by Leist by the repeated washing of the acid sulphate with water. Hensgen could not obtain this salt.

$3Bi_2O_3.2SO_3.3H_2O$ is obtained by heating a solution of bismuth nitrate with sodium sulphate in a closed tube at 200° to 250° (Athanasesco[1]).

In this research acid bismuth sulphate or the basic salt prepared by stirring the acid sulphate with 10 per cent sulphuric acid, was stirred with sulphuric acid solutions of different concentrations till equilibrium was reached. The apparatus used was the same as that described in this JOURNAL, **25**, 307 (1901). For that part of the series near the point at which both basic sulphates are present, the reaction was very slow and required six weeks for completion. Where the liquid contained little sulphuric acid, the composition of the solid phase was deduced from the change in the liquid, but the solids in equilibrium with the stronger acid solutions were analyzed directly, after being rubbed between porous plates. Great difficulty was found in freeing the salt from the adhering sulphuric acid, and the analyses, as a rule, show values for sulphuric anhydride which are slightly too high.

In the following table, the second column contains the composition of the liquid phases in the different bottles, at equilibrium, expressed in percentages of sulphuric acid, or with reference to a normal solution. The third column shows the composition of the solid contents:

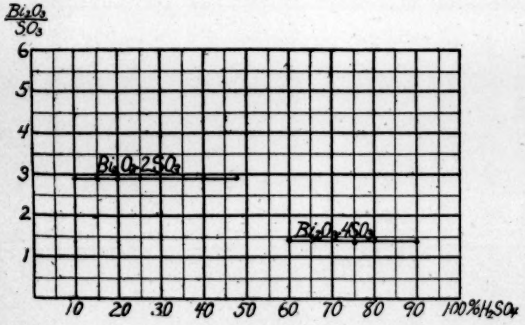
$\frac{Bi_2O_3}{SO_3}$ in $Bi_2O_3.4SO_3 = 1.45$.
" " $5Bi_2O_3.11SO_3 = 2.64$.
" " $Bi_2O_3.2SO_3 = 2.90$.
" " $Bi_2O_3.SO_3 = 5.80$.

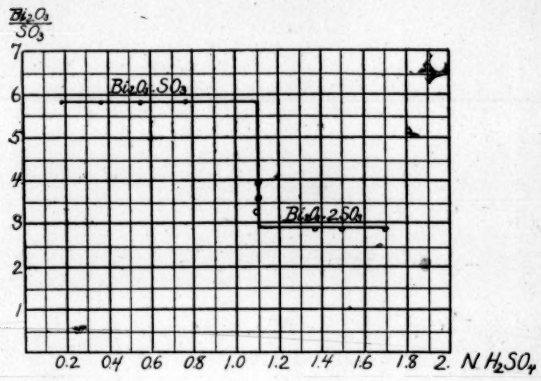
Temperature 50°.

[1] Compt. rend., **103**, 171.

No.	Composition of liquid. Per cent H_2SO_4.	$\frac{Bi_2O_3}{SO_3}$ in solid.
1	90	1.36
2	80	1.43
3	75	1.38
4	65	1.45
5	60	1.47
6	51.4	2.21
7	47.5	2.84
8	40	2.89
9	25	2.84
10	20	2.86
11	15	2.85
12	10	2.90
	N.H_2SO_4.	
13	9 = 1.7	2.87
14	1.51	2.85
15	1.37	2.88
16	1.09	3.27
17	1.11	3.61
18	1.11	3.91
19	0.77	5.78
20	0.55	5.77
21	0.36	5.77
22	0.18	5.79

These results may be represented in two diagrams, in each of which the composition of the solid contents is represented by one axis, and the composition of the liquid by the other, but in the second, which includes Nos. 13 to 22, a different scale is used in representing the composition of the liquid phase:





It will be seen that Nos. 1 to 5 have but one solid phase, $Bi_2O_3.4SO_3$, Nos. 7 to 15 contain $Bi_2O_3.2SO_3$, and Nos. 19 to 22 contain $Bi_2O_3.SO_3$. Nos. 16 to 18 have liquid phases of the same composition and two solid phases, $Bi_2O_3.2SO_3$ and $Bi_2O_3.SO_3$.

The salt obtained from Nos. 19 to 22 was stirred with water, at 50° for twelve days, and sulphuric acid could not be detected in the liquid.

The amount of water in the acid salt was not determined. A specimen of $Bi_2O_3.2SO_3$ dried between paper gave results agreeing with the formula $Bi_2O_3.2SO_3.2\frac{1}{2}H_2O$.

	Calculated for $Bi_2O_3.2SO_3.2\frac{1}{2}H_2O$.	Found.
Bi_2O_3	69.42	69.40
SO_3	23.87	23.90

This salt lost only a trifling amount when heated to 100°.

Summary.

1. At 50° acid bismuth sulphate is in equilibrium with sulphuric acid solutions from 51.4 per cent up, $Bi_2O_3.2SO_3.2\frac{1}{2}H_2O$ with acid solutions between 1.1 normal (= 5.4 per cent) and 51.4 per cent, and $Bi_2O_3.SO_3$ with acid solutions weaker than 1.1 normal.

2. $Bi_2O_3.SO_3$ is not acted on by water at 50°.

3. The salt $5Bi_2O_3.11SO_3.17H_2O$ described by Adie was not obtained.

CHEMICAL LABORATORY, UNIVERSITY OF TORONTO, January, 1902.

Contribution from the North Carolina Experiment Station.

[Communicated by W. A. Withers.]

THE SOLUBILITY OF BARIUM SULPHATE IN FERRIC CHLORIDE, ALUMINIUM CHLORIDE, AND MAGNESIUM CHLORIDE.

BY G. S. FRAPS.

In working on the determination of sulphuric acid in soils, Mr. C. B. Williams, assistant chemist to the North Carolina Department of Agriculture, found that considerably more barium sulphate was obtained when the iron and aluminium had been previously precipitated from the soil solution.[1] This led to the following work.

The latest determinations of the solubility of barium sulphate which have been made are those of R. Fresenius and E. Hintz,[2] in which the solubility was determined in pure water, 2.5 and 10 per cent ammonium chloride, 2.5 per cent sodium chloride, 10 per cent nitric acid, and 10 per cent hydrochloric acid, alone, and in the presence of an excess of sulphuric acid or barium chloride.

In regard to the effect of ferric salts, aluminium salts, and magnesium salts upon its solubility, we have few data. Fresenius states that its solubility in water is increased by the presence of magnesium chloride, and Lunge[3] states that it is soluble in ferric chloride. As the precipitation of barium sulphate sometimes take place in the presence of these salts, the knowledge of its solubility is important in analytical work.

Method of Work.

The method used was similar to that adopted by R. Fresenius,[4] barium chloride being used in place of barium hydroxide.

[1] His results are not yet published.

[2] Ztschr. anal. Chem., **35**, 170 (1896).

[3] *Ibid.*, **19**, 431.

[4] *Loc. cit.*

A solution of barium chloride was prepared, 100 cc. of which was found to give 0.0952 and 0.0945 gram barium sulphate, *i. e.*, 1 cc. = 0.95 milligram $BaSO_4$. A solution of sulphuric acid was prepared, 100 cc. of which gave 0.1206 and 0.1204 gram barium sulphate, or 1 cc. was equal to 1.2 milligrams barium sulphate.

Preliminary tests were then made upon solutions of ferric chloride, aluminium chloride, and magnesium chloride. 400 cc. of the solutions were placed in precipitating jars and sulphuric acid and barium chloride solution were added in the proper proportions to make 10 milligrams barium sulphate. The solution was allowed to stand twenty-four hours, and if no precipitate appeared 10 milligrams more of barium sulphate were added, and so on until a precipitate appeared.

More exact tests were then made, based upon the results of the preliminary tests. In making these tests, the solution was allowed to stand forty-eight hours instead of twenty-four, as it was found that precipitates sometimes appeared during the second twenty-four hours. Much smaller quantities of barium sulphate were added each time, and the very faintest trace of appearance of barium sulphate was watched for. It was found that if the stirring-rod was rubbed against the sides of the vessel the barium sulphate separated out at this point more rapidly and more readily than elsewhere, and could be easily seen. In making up the solutions of the various salts, allowance was made for the quantity of water which would probably be added with the barium chloride and sulphuric acid.

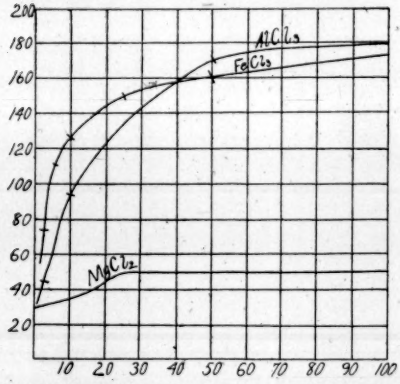
Results of Work.

The solubility of nascent barium sulphate in the solution of chlorides of different concentrations is given in the following table. Neither barium chloride nor sulphuric acid was present in excess in any case.

Solubility of Barium Sulphate.

Amount of salt per liter. Grams.	$BaSO_4$ dissolved per liter. Milligrams in $FeCl_3$.	$AlCl_3$.	$MgCl_2$.
1	58	33	30
2½	72	43	30
5	115	60	33
10	123	94	33
25	150	116	50
50	160	170	50
100	170	175	50

Solubility Curves of Barium Sulphate.



Comparing these figures with the results of Fresenius with other salts, we find that barium sulphate is much less soluble in 10 per cent ferric chloride, or aluminium chloride, than in 10 per cent nitric acid, or hydrochloric acid. It is also more readily soluble in a 10 per cent solution of ammonium chloride than in ferric chloride or aluminium chloride, of the same strength, though less soluble in 2.5 per cent ammonium chloride.

Solubility in Presence of Barium Chloride.

The solubility of barium sulphate in ferric chloride and

aluminium chloride in the presence of barium chloride in excess was tested in the same way as before. The results are as follows. In each case 12.5 milligrams barium sulphate per liter were present (5 milligrams in 400 cc.):

With 5 grams aluminium chloride and 7.5 cc. of barium chloride (1 : 10) per liter present, the solution became turbid in an hour.

With 10 grams aluminium chloride and 20 cc. barium chloride the solution became turbid in an hour.

With 25 grams aluminium chloride and 12.5 cc. barium chloride a very faint precipitate appeared in forty-eight hours.

With 5 grams ferric chloride, 7.5 cc. barium chloride, a slight precipitate appeared in twenty-four hours.

With 10 grams ferric chloride, 20 cc. barium chloride, a slight precipitate appeared in twenty-four hours.

With 25 grams ferric chloride and 12.5 cc. barium chloride a very faint precipitate appeared in forty-eight hours.

Comparing these results with those of Fresenius, we find that, in the presence of barium chloride, barium sulphate is less soluble in ferric chloride, or aluminium chloride, than in a 10 per cent, or 2.5 per cent, solution of ammonium chloride, or in a 2.5 per cent solution of sodium chloride, or nitric acid, or hydrochloric acid.

RALEIGH, N. C., February, 1902.

I. AN INVESTIGATION OF THE FATTY OIL CONTAINED IN THE SEEDS OF LINDERA BENZOIN.

II. LAURIC ACID AND SOME OF ITS DERIVATIVES.[1]

BY CHARLES E. CASPARI.

Stillman and O'Neill[2] undertook an investigation of the fatty oil contained in the fruit of the California bay tree, *Umbellularia Californica* or *Laurus Californica*, and isolated a new acid, $C_{11}H_{22}O_2$, which they called umbellulic acid. This acid is one of the few exceptions to the general rule that of

[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1900, for the degree of Doctor of Philosophy.

[2] This JOURNAL, 4, 206.

the higher members of the fatty acid series only those occur in nature which contain an even number of carbon atoms. This new acid differs quite markedly from the isomeric undecylic acid, $C_{11}H_{22}O_2$, obtained by Krafft. However, very little is known about umbellulic acid, as no work has been done on it since the publication of the article referred to above.

It was thought possible that, since the *Lindera Benzoin* belongs to the same family as the California bay tree, it might also contain umbellulic acid or some acid closely related to it, and it was with this possibility in mind that the present investigation was undertaken.

While it has not been possible to isolate umbellulic acid or indeed any acid containing an uneven number of carbon atoms, nevertheless, some interesting results have been obtained.

Lindera Benzoin, also known as *Benzoin odoriferum* and *Laurus Benzoin*, and commonly called spicewood, spicebush, or feverbush, is a bush growing to the height of 20 feet, frequently much lower, and is indigenous all over the United States. It is found chiefly in damp regions along water courses, and is quite generally used in the southern states by the country people as a remedy against fever and measles. It has a strong odor of spices and contains an ethereal oil in all of its parts.[1]

The oil of its bark and twigs has the odor of wintergreen, boils between 170° and 300°, has the sp. gr. 0.923 and contains 9 to 10 per cent of methyl salicylate. The oil from the berries contains about 4 per cent of an oil with a camphoraceous odor, the sp. gr. 0.850 to 0.855, which boils from 160° to 270°. The leaves contain about 0.3 per cent of an oil having the odor of lavender and the sp. gr. 0.888.

In this investigation only the oil from the berries has been dealt with. In the neighborhood of Baltimore, where the material was collected, the berries ripen in the middle or latter part of September, and must be gathered very soon after they ripen, otherwise they will fall to the ground and be lost in the undergrowth.

When ripe the berries have a bright-red color, are oval in shape and are about a half inch long. A half bushel of these

[1] Report of Schimmel & Co., October, 1885, p. 27, and October, 1890, p. 49.

were collected in Howard County, Maryland, and were steeped in water for several days until the outer flesh or pulp began to soften and decay. It was then comparatively easy to obtain the inner kernel entirely free from the softer pulp. The kernels were allowed to dry completely in the air. The half bushel of berries yielded about 2,500 grams of kernels.

The investigation is divided into two parts: first, the examination of the oil from the berries, and second, a thorough investigation of lauric acid, which was found in the oil as a glyceride, and of some of its derivatives.

Examination of the Oil Contained in the Berries of the Lindera Benzoin.

A few grams of the kernels were thoroughly macerated, mixed with ether, and extracted for several hours in a Soxhlet extractor. The ether was evaporated from the solution, the residue mixed with water and subjected to distillation with steam. An extremely small amount of oil distilled over, which contained all the odorous material of the oil, since the residue after distillation was entirely odorless. However, the amount of volatile oil was so very small that it was impossible to obtain enough of it from the amount of material at hand for investigation, and so the work was confined to that portion of the oil which is not volatile with water vapor. It is hoped at some later day to complete the examination of the volatile oil.

A quantitative determination of the oil contained in the seeds gave the following result:

3.2809 grams seeds yielded 1.9065 grams oil, which is equivalent to 58.10 per cent.

This result is a trifle too high, because it was impossible to prevent a small amount of the finely divided pulp from filtering through the paper thimble of the Soxhlet extractor, and this pulp was then weighed with the oil, but the error is only a very small one.

Some difficulty was experienced in obtaining a satisfactory method for extracting the oil from the seeds.

It was first attempted to extract all the material with ether in a Soxhlet extractor, but this method was unsatisfactory

for two reasons. In the first place, some of the pulp was always present in the oil, and it was practically impossible to filter it off; and in the second place, the extractors at hand were so small that it would have entailed a great loss of time to have extracted all the seeds in that way. It was then attempted to moisten the macerated pulp with ether, and express the mass in a hand press which was available. This method gave the oil free from pulp, but the yield was only about 60 per cent of what it should have been. Finally, Professor Remsen wrote to Messrs. Fritzsche Brothers, in Garfield, New Jersey, asking them whether they would extract the seeds for us. They very kindly consented to do so, and I take this opportunity of thanking them for their kindness. They expressed the seeds, and then extracted the expressed mass with petroleum ether boiling at 40° to 50°. After evaporating the petroleum ether, the extracted and expressed oils were distilled with steam for several hours, but the amount of volatile oil was so small that they did not consider it worth the trouble of isolating it. From 2130 grams of the seeds were obtained

735 grams = 34.5 per cent of expressed oil,
237 grams = 11.1 per cent of extracted oil.
Total: 972 grams = 45.6 per cent.

The product obained from Messrs. Fritzsche Brothers was a solid fat. It was yellow and quite crystalline throughout its structure. It melted at 26°. The fat is very soluble in ethyl alcohol, benzene, gasoline, and acetone, but is more difficultly soluble in anhydrous methyl alcohol. Its solution in ethyl alcohol reacts neutral towards litmus.

1.9311 grams fat require for saponification 0.5492 gram caustic potash. Hence 1 gram fat requires 284.4 milligrams caustic potash for saponification.

Volatile and Soluble Acids.—The saponified material obtained in the above determination was used for this determination. The alcohol was evaporated and the potassium salts were dissolved in water. The fatty acids were set free by dilute sulphuric acid. After diluting with water, the mixture was distilled so that 110 cc. of distillate were obtained in a

half hour. This distillate was then filtered and titrated with N/10 caustic potash, using phenolphthalein as an indicator. The amount of alkali required for neutralization was 0.998 cc. The weight of fat used was 1.9311 grams. Therefore, 2.5 grams of fat would require 1.29 cc. N/10 caustic potash to neutralize the volatile and soluble acids contained in it. Hence the Reichert number is 1.29. Another determination gave the value 1.34.

These results show that the percentage of volatile and soluble acids obtained from the fat is very small, and they doubtless consist of small amounts of capric acid, $C_{10}H_{20}O_2$, which was later found in the fat as the glyceride, and which is volatile with steam and slightly soluble in water.

While the distillation was in progress in determining the Reichert number, it was noticed that a small amount of some material came over, which was insoluble in water and solid at ordinary temperatures. Some of this material was collected and dissolved in alcohol, and this solution reddened blue litmus paper. The solution was heated to boiling, and to it was added a hot solution of lead acetate in alcohol. Very soon fine, delicate needles, clustering together in rosettes, appeared, and when the solution had cooled these were filtered off, washed well with water and with alcohol, and dried over calcium chloride. Analysis of the salt yielded the following results:

I. 0.1460 gram salt gave 0.0757 gram $PbSO_4$.
II. 0.3128 gram salt gave 0.1581 gram $PbSO_4$.

	Calculated for $Pb(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Pb	34.17	35.34	34.52

The barium salt of the same acid was made by treating a boiling alcoholic solution of the acid with a boiling alcoholic solution of barium acetate. The salt was washed, dried over calcium chloride, and analyzed with the following results:

I. 0.2629 gram salt gave 0.1157 gram $BaSO_4$.
II. 0.2203 gram salt gave 0.0971 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ba	25.64	25.87	25.92

From the above analytical results it would seem that the acid was lauric acid, which is difficultly volatile with water vapor and which is insoluble. However, through subsequent work this conclusion was shown to be wrong, and the explanation of the above results will be given further on.

To make sure that the barium salt mentioned above was a salt of lauric acid alone, it was subjected to fractional crystallization from water, in which it is quite insoluble.

Two or three grams of the barium salt were boiled with two liters of water. A portion of it dissolved and was filtered boiling hot. Immediately crystals began to separate out, and after about fifteen minutes these were filtered off, dried, and analyzed.

0.1836 gram salt gave 0.0805 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found.
Ba	25.65	25.75

When the above filtrate had cooled to the temperature of the room, more crystals had separated out. These were filtered off, dried over calcium chloride, and analyzed.

0.1340 gram salt gave 0.0611 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Calculated for $Ba(C_{11}H_{21}O_2)_2$.	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found.
Ba	25.65	27.06	28.64	26.84

The filtrate from the second crop of crystals was concentrated considerably by evaporation, and when the solution had cooled crystals again separated out. After drying over calcium chloride they were analyzed.

0.2582 gram salt gave 0.1237 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found.
Ba	28.64	28.20

Next, the crystals which were found to contain 26.84 per cent of barium were dissolved in boiling water, and the solution was allowed to cool to the temperature of the room. The crystals which separated out were dried and analyzed.

0.2306 gram salt gave 0.1017 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found.
Ba	25.65	25.95

The filtrate from these crystals was evaporated down, and, upon cooling, a second crop of crystals separated out. These were likewise dried and analyzed.

0.1994 gram salt gave 0.0959 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found.
Ba	28.64	28.32

Finally, that portion of the original barium salt which was insoluble in boiling water was boiled with more water and went completely into solution. It had not dissolved before because there had not been enough water present. Almost as soon as boiling ceased crystals began to separate out quite rapidly, and these were filtered off while the solution was still quite hot. After drying over calcium chloride they gave the following result upon analysis:

0.2589 gram salt gave 0.1114 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found.
Ba	25.65	25.33

The filtrate from these crystals, when cooled down to the temperature of the room, did not deposit enough crystals for an analysis, and when concentrated considerably by evaporation, and cooled, not enough material for analysis separated out.

This fractional crystallization of the barium salt offers very strong evidence in favor of the fact that the material which is volatile with steam and insoluble in water, obtained when the mixed acids derived from the fat are distilled with steam, consists not of lauric acid alone, but of lauric and capric acids. Of the first three fractions obtained, the first one approximates very closely to barium laurate, the third one to barium caprate, while the second one gives an analysis which agrees very well with that demanded by barium undecylate, $Ba(C_{11}H_{21}O_2)_2$, but the second one, when redissolved and subjected to fractional crystallization, can be resolved into two salts whose barium content agrees very well with that of barium laurate and barium caprate. Finally, that portion of the original barium salt which remained undissolved, when it was first boiled with water, dissolved completely when more water was added, and

upon crystallization yielded practically only barium laurate. This can be explained only if barium laurate and barium caprate were originally present. The first time the barium salt was boiled with water, a large part of the barium laurate and all of the barium caprate went into solution, because barium caprate is much more soluble in water than barium laurate, and the residue which dissolved completely when boiled again with water consisted entirely of barium laurate, and did not dissolve at first on account of its great insolubility in water.

It now seems clear why the lead and barium salts described on page 295 gave analytical results agreeing so well with those of barium laurate and lead laurate. Evidently, in each case, lead acetate and barium acetate had been added in quantities insufficient to precipitate the acids completely. Only the lead and barium laurates crystallized out with perhaps a very little of the caprates, because the caprates are so much more soluble than the laurates in alcohol, as well as in water.

The fractional crystallization of the barium salt of the mixed acids, and the subsequent liberation of the free acids from their separated salts does not offer a very expedient method for the separation of the pure acids, because such an enormous amount of water is required to dissolve the original barium salts. Hence it was thought best to saponify the fat, liberate the free acids, and subject them to fractional distillation under diminished pressure. In this way it is possible to separate the individual acids quite thoroughly.

Accordingly, about 250 grams of the fat obtained from Fritzsche Brothers were saponified with an alcoholic solution of potassium hydroxide (66 grams to the liter). After the alcohol was distilled from the saponified material, there was left a dark-brown, pasty mass, which consisted of the potassium salts of the fatty acids, together with any glycerol which might have been present in the fat in the form of glycerides. This dark residue was dissolved completely in cold water, and from this solution the free acids were precipitated by means of dilute sulphuric acid. They are solid at ordinary temperatures, and float on the aqueous solution. The entire mass was heated on the water-bath until the acids had melted and had collected completely at the surface. Upon cooling, the

acids formed a solid cake, which could be easily lifted off from the aqueous solution. This aqueous solution was filtered, neutralized with potassium hydroxide, and evaporated almost to dryness. The residue was extracted five times with absolute alcohol, and this alcoholic solution was afterwards examined for glycerol. The fatty acids were heated on the water-bath for ten to twelve hours in order to dry them as much as possible before distilling them.

The apparatus used for distillation under diminished pressure was that recommended by Anschütz. It consisted of two distilling bulbs, the side tube of one fitting into the neck of the other, which was the receiver. The side tube of the receiver was connected with a manometer, which in turn was connected with an ordinary filter-pump. Only rubber stoppers and very thick-walled rubber tubing were used in making connections. A capillary tube, through which a small current of air was constantly kept passing, dipped under the surface of the boiling liquid rendering the ebullition more regular, and preventing any liquid which was not first vaporized from passing over into the receiver. The distilling bulb was never more than one-third filled, and was placed in an iron dish, the bottom of which was covered with fine asbestos, so that the bulb could not come in contact with the metal, and then heat was applied to the iron dish. The temperature of the air-bath was never allowed to rise more than 40° higher than the temperature of the vapor in the distilling bulb. No condenser tube was necessary, since the acids boiled so high that the side tube of the distilling bulb was sufficiently long to condense all the vapors.

Under 11 to 15 mm. pressure, the acids which had been dried on the water-bath, began to boil at 150°, and from the first distillation two fractions were collected, from 150° to 170° and from 170° to 185°. The portion boiling above 185° was reserved for examination later on. These two fractions were then redistilled and three fractions were collected under 12 to 14 mm. pressure, from 154° to 157°, from 157° to 166°, and from 166° to 187°. In the last fraction most of the distillate came over at about 168°. During the distillation the temperature of the air-bath varied from 190° to 220°. The first and

third fractions contained approximately equal volumes, while the volume of the intermediate fraction was much smaller than that of the first or third. These three fractions were colorless when liquid and white when solid, with a decidedly crystalline structure. The barium salts of the acids in the first and third fractions were made by bringing together a boiling alcoholic solution of the acid with a concentrated boiling solution of barium acetate in about 50 per cent alcohol. After being washed with alcohol and with water and dried in the air, these salts were analyzed for barium with the following results:

Fraction boiling from 154° to 157° under 12 to 14 mm. pressure.

I. 0.2144 gram salt gave 0.1025 gram $BaSO_4$.
II. 0.2321 gram salt gave 0.1107 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found. I.	II.
Ba	28.64	28.15	28.08

Fraction boiling from 166° to 187° under 12 to 14 mm. pressure.

I. 0.2935 gram salt gave 0.1281 gram $BaSO_4$.
II. 0.2918 gram salt gave 0.1274 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ba	25.65	25.69	25.70

From these results the conclusion may be drawn that the fraction boiling from 154° to 157° consisted mainly of capric acid with perhaps a very little lauric acid, and that the fraction boiling from 166° to 187° consisted of quite pure lauric acid.

In order to obtain a purer capric acid, the fraction boiling from 154° to 157° was redistilled, together with the intermediate fraction mentioned above, which, under the same pressure, boiled from 157° to 166°. From this distillation three fractions were obtained, the first boiling from 156° to 157° under 15 mm. pressure, the second boiling from 150° to 154° under 10 to 11 mm. pressure, and the third from 157° to 169° under 13 mm. pressure. The first fraction had by far the largest volume, while the second and third fractions each had

a volume which was much smaller than that of the fraction boiling from 157° to 166° under 10 to 12 mm. pressure. These facts show that this last-mentioned fraction was composed of a lower and a higher boiling portion. The analyses below show that it consisted of a mixture of capric and lauric acids.

The barium salts of the three new fractions were made exactly as those described above, and upon analysis gave the following results for barium :

Fraction boiling from 156° to 157° under 15 mm. pressure.

I. 0.2007 gram salt gave 0.0965 gram $BaSO_4$.

II. 0.2315 gram salt gave 0.1115 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	Found. I.	II.
Ba	28.64	28.31	28.35

Fraction boiling from 150° to 154° under 10 to 11 mm. pressure.

I. 0.2656 gram salt gave 0.1254 gram $BaSO_4$.

II. 0.2017 gram salt gave 0.0948 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	$Ba(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ba	28.64	25.65	27.76	27.67

Fraction boiling from 157° to 169° under 13 mm. pressure.

I. 0.2240 gram salt gave 0.0997 gram $BaSO_4$.

II. 0.2573 gram salt gave 0.1148 gram $BaSO_4$.

	Calculated for $Ba(C_{10}H_{19}O_2)_2$.	$Ba(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ba	28.64	25.65	26.20	26.27

Thus, the first fraction consists of practically pure capric acid, the second fraction of capric acid with a little lauric acid, and the third fraction of lauric acid with a very much smaller amount of capric acid. From this it appears evident that no acid of the formula $C_{11}H_{22}O_2$ was present, a conclusion also arrived at from the evidence presented by the fractional crystallization of the barium salts of the mixed acids, when the barium salt containing 26.84 per cent of barium, the percentage of barium in the barium salt of $C_{11}H_{22}O_2$ being 27.06, was resolved into barium caprate and barium laurate.

A small portion of the residue boiling above 185° under 11 to 15 mm. pressure was dissolved in chloroform and treated

with bromine water. The color of the bromine disappeared immediately, showing the presence of some unsaturated acid. To test whether this acid was formed during the distillation by decomposition from lauric and capric acids, some of the original fat was treated in solution in chloroform with bromine water, and again the color disappeared immediately, showing that the unsaturated compound was present as such in the original fat. The high-boiling residue was distilled under 10 mm. pressure. Up to 218° very little distillate was obtained, and this was doubtless impure lauric acid, as it solidified almost immediately. From 218° to 225° a very appreciable amount of a clear liquid distilled over, and above 225° the mass carbonized. The distillate which came over between 218° and 225° melted at 13°, the melting-point of oleic acid being given as 14°. A hot alcoholic solution of the acid, which did not redden blue litmus paper, another characteristic of oleic acid, was treated with ammonium hydroxide and barium chloride, and filtered hot. Upon cooling, a voluminous white crystalline precipitate separated out, which, upon analysis, gave the following results:

I. 0.2372 gram salt gave 0.0786 gram $BaSO_4$.
II. 0.2147 gram salt gave 0.0710 gram $BaSO_4$.

	Calculated for $Ba(C_{18}H_{33}O_2)_2$.	Found. I.	II.
Ba	19.63	19.51	19.47

These results point to the conclusion that the acid boiling from 218° to 225° under 10 mm. pressure is oleic acid. Krafft and Nordlinger[1] give 223° as the boiling-point of oleic acid under 10 mm. pressure. Another piece of evidence also showed that oleic acid is contained in the fat. It is well known that lead oleate is soluble in ether, while the lead salts of the saturated acids are not. Accordingly, the potassium salts of the mixed acids from the fat were treated in aqueous solution with a solution of lead acetate. A copious, white, creamy precipitate was immediately thrown down, and was filtered off and dried as well as possible in the air. It was then extracted with ether several times, and the solution in ether was evaporated down considerably when a yellowish

[1] Ber. d. chem. Ges., **22**, 819.

crystalline mass separated out. This mass was recrystallized from ether, and was finally obtained as a white crystalline powder, which melted at about 80° to a yellow liquid. Upon analysis for lead it gave the following results:

I. 0.2437 gram salt gave 0.0953 gram $PbSO_4$.
II. 0.2156 gram salt gave 0.0845 gram $PbSO_4$.

	Calculated for $Pb(C_{18}H_{33}O_2)_2$.	Found. I.	II.
Pb	26.88	26.69	26.75

These two pieces of evidence—one from the acids after distillation, the other from the crude acids—leave little doubt that oleic acid is contained in the original fat.

It will be remembered that when the fat had been saponified and the acids set free, the aqueous filtrate from the acids was neutralized with potassium hydroxide, evaporated almost to dryness, and that the residue was extracted several times with absolute alcohol. This alcoholic solution was then examined for glycerol. The alcohol was evaporated off and there was left a thick, viscous liquid, quite sweet to the taste. This was heated to 170° in order to drive off all traces of alcohol and water. Portions of this residue were heated in a test-tube with about twice their mass of acid potassium sulphate when the disagreeable penetrating vapors of acrolein were evolved, proving that the thick liquid above mentioned was glycerol.

It is clear from the results here given that the fatty oil or fat of the seeds of the *Lindera Benzoin* consists of a mixture of the glycerides of capric, lauric, and oleic acids. No quantitative determinations of the amount of each acid present were made, but the lauric acid is present in largest proportion.

LAURIC ACID AND SOME OF ITS DERIVATIVES.

Lauric acid was discovered in 1842 in Liebig's laboratory by Marsson.[1] He obtained it by saponifying the fat contained in laurel berries, and called it laurostearic acid. The acid with which he worked melted at 42° to 43°. Sthamer[2] obtained lauric acid by saponification of the fat contained in

[1] Ann. Chem. (Liebig), **41**, 329.
[2] *Ibid.*, **83**, 390.

pichurim beans from South America. His acid melted at 43°. A few years later Görgey,[1] during an extensive investigation of cocoanut oil, found that it contained lauric acid. Capric and caprylic acids were also present, and he separated the three acids by fractional crystallization of their barium salts. He described lauric acid very much as Marsson and Sthamer had done, and said it melted at 42° to 43°. Heintz[2] obtained lauric acid, which melted at 43°.6, from whale fat. In 1867, Oudemans[3] found lauric acid as a constituent of Fangkallak fat obtained from the *Cylicodaphne sebifera*, of Java. Oudemans,[4] in 1863, prepared and described several of the salts of lauric acid. He did not state the source or the melting-point of his acid, and since many of his results differ considerably from those obtained with the lauric acid from the seeds of *Lindera Benzoin*, it is questionable whether Oudemans was dealing with perfectly pure lauric acid. As most of the work on lauric acid was done more than forty years ago, it seemed desirable that some of the work should be repeated with the aid of modern improvements in chemical methods.

The method of obtaining lauric acid from the seeds of *Lindera Benzoin* has already been described. The acid melts at 42° and boils at 166° under 10 to 11 mm. pressure. It is very soluble in alcohol, from which it can be crystallized in warty crystals, which have a satin luster. It is practically insoluble in water. In alcoholic solution it turns blue litmus paper red. Upon analysis the acid gave the following results:

I. 0.2432 gram acid gave 0.6398 gram CO_2 and 0.2662 gram H_2O.

II. 0.2314 gram acid gave 0.6083 gram CO_2 and 0.2557 gram H_2O.

	Calculated for $C_{12}H_{24}O_2$.	Found. I.	II.
C	71.91	71.75	71.69
H	12.10	12.17	12.27

In order to be sure that this acid is identical with that ob-

[1] Ann. Chem. (Liebig), **66**, 290.
[2] *Ibid.*, **92**, 294.
[3] Ztschr. Chem., 1867, p. 256.
[4] J. prakt. Chem., **89**, 206.

tained by Krafft[1] from laurel oil, from whose results those here given differ somewhat, a half kilogram of laurel oil was purchased from Dodge and Olcott, in New York, which yielded about 10 per cent of lauric acid by saponification and distillation under diminished pressure. This acid melted at 42° and boiled at 166° under 11 mm. pressure, and was in all respects identical with that obtained from the seeds of the *Lindera Benzoin*. Krafft said that his acid melted at 43°.5.

Of the sources of lauric acid thus far discovered, the seeds of the *Lindera Benzoin* yield it most abundantly and with comparatively little difficulty.

The Chloride of Lauric Acid, $C_{11}H_{23}.CO.Cl$.—The chloride[2] of the acid was made by treating the melted acid with a little more than the calculated amount of phosphorus trichloride and heating the mixture on the water-bath for fifteen or twenty minutes, until the action was complete. In this reaction only the chloride of the acid and phosphorous acid are formed. The latter sinks to the bottom of the dish as a rather viscous liquid, so that the chloride can be poured from it very easily. In order to purify this crude chloride, it was subjected to distillation under diminished pressure, and after one distillation it yielded the following analytical results:

I. 0.3772 gram chloride gave 0.2447 gram AgCl.

II. 0.2264 gram chloride gave 0.1474 gram AgCl.

	Calculated for $C_{11}H_{23}.COCl$.	Found. I.	Found. II.
Cl	16.21	16.04	16.09

The chloride is decomposed slowly by the moisture in the air, and must hence be well protected from the air. It is also decomposed very quickly by alcohol. According to Krafft[3] it boils at 142°.5 under 15 mm. pressure and melts at —17°. That which gave the above results boiled at 145° under 18 mm. pressure, and remained liquid when cooled down to —17°.

The Amide of Lauric Acid, $C_{11}H_{23}.CONH_2$.—The amide of lauric acid was made according to the method for the general preparation of acid amides recommended by Aschan.[4] It was

[1] Ber. d. chem. Ges., **12**, 1664.
[2] *Ibid.*, **31**, 2344.
[3] *Ibid.*, **17**, 1378.
[4] *Ibid.*, **31**, 2344.

his method that was used in making the acid chloride. The chloride was added, drop by drop, to an excess of a well-cooled, concentrated solution of ammonia, which was constantly stirred. The amide was precipitated out immediately, as it is insoluble in water. It was crystallized several times from 50 per cent alcohol until its melting-point remained constant after three crystallizations. The amide crystallizes in very fine, feathery, white needles, which, when dry, have a very fluffy appearance with a satin luster. It melts sharply between 98° and 99°. Upon analysis it gave the following results:

0.1689 gram amide gave 0.4492 gram CO_2 and 0.1938 gram H_2O.

	Calculated for $C_{11}H_{23}.CONH_2$.	Found.
C	72.26	72.53
H	12.67	12.73

0.3202 gram amide gave 0.0228 gram N.

	Calculated for $C_{11}H_{23}.CONH_2$.	Found.
N	7.02	7.13

The nitrogen was determined as ammonia by the Kjeldahl method.

The amide of lauric acid has been made only once before, and then by Krafft.[1] He does not give any analyses of his product nor does he say how he purified it. His amide melted at 102°.

The Anilide of Lauric Acid, $C_{11}H_{23}.CO.NH.C_6H_5$.—This was made by adding the chloride, drop by drop, to an emulsion in water of twice the calculated amount of aniline required. The product of the reaction was crystallized several times from 50 per cent alcohol, and finally it melted constantly before and after two crystallizations at 76°.5. The anilide crystallizes quite well in long, feathery, fluffy, white needles, resembling finely shredded asbestos. It was analyzed for nitrogen by the Kjeldahl method with the following result:

0.2548 gram anilide gave 0.0133 gram N.

	Calculated for $C_{11}H_{23}.CO.NH.C_6H_5$.	Found.
N	5.10	5.20

[1] Ber. d. chem. Ges., **15**, 1729.

The o-Toluide of Lauric Acid, $C_{11}H_{23}.CO.NH.C_6H_4.CH_3$.—This forms very fine, light, white needles, which melt at 81°.5. A determination of nitrogen yielded the following result by the Kjeldahl method.

0.2496 gram toluide gave 0.0119 gram N.

	Calculated for $C_{11}H_{23}.CO.NH.C_6H_4.CH_3$.	Found.
N	4.84	4.78

The amide, anilide, and toluide of lauric acid resemble each other very closely in appearance and in their solubility. They are all insoluble in water and easily soluble in 95 per cent alcohol. The best menstruum from which to crystallize them is 50 per cent alcohol.

Barium Laurate, $Ba(C_{12}H_{23}O_2)_2$.—Barium laurate was made by bringing together a boiling solution of lauric acid in 95 per cent alcohol and a boiling solution of barium acetate in 50 per cent alcohol. Almost immediately after mixing the two solutions the crystals of barium laurate separated out. They consist of very fine, white needles, arranged in the form of rosettes. These, when dry, have a luster resembling that of mother of pearl or of fish scales.

Barium laurate is very difficultly soluble in water and in alcohol, and does not melt when heated to 260°. It yielded the following analytical results for barium:

I. 0.4751 gram salt gave 0.2061 gram $BaSO_4$.

II. 0.4351 gram salt gave 0.1897 gram $BaSO_4$.

	Calculated for $Ba(C_{12}H_{23}O_2)_2$.	Found. I.	Found. II.
Ba	25.64	25.54	25.66

Oudemans[1] describes barium laurate as amorphous, while as a matter of fact it is quite crystalline.

Strontium Laurate, $Sr(C_{12}H_{23}O_2)_2 + H_2O$.—Strontium laurate was made by mixing a boiling solution of lauric acid in 95 per cent alcohol with a boiling solution of strontium acetate in 50 per cent alcohol. Before the solution had cooled crystals of strontium laurate separated out. These consisted of fine, white needles, which clustered together, but did not have the pearly luster of barium laurate. Strontium laurate

[1] J. prakt. Chem., 89, 206.

is as insoluble in water as barium laurate and nearly as insoluble in alcohol. It decomposes, without melting, at about 240° and contains 1 molecule of water of crystallization.

I. 0.2177 gram salt gave 0.0076 gram H_2O.
II. 0.2236 gram salt gave 0.0077 gram H_2O.

	Calculated for $Sr(C_{12}H_{23}O_2)_2 + H_2O$.	Found. I.	II.
H_2O	3.57	3.51	3.48

I. 0.2101 gram anhydrous salt gave 0.0790 gram $SrSO_4$.
II. 0.2159 gram anhydrous salt gave 0.0811 gram $SrSO_4$.

	Calculated for $Sr(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Sr	18.02	17.96	17.93

Calcium Laurate, $Ca(C_{12}H_{23}O_2)_2 + H_2O$.—Calcium laurate was made like the barium and strontium salts. It is much more soluble in alcohol than either of these salts and crystallizes in very short, delicate, white needles, which cannot be distinctly seen without the aid of a pocket lens. The crystals contain one molecule of water of crystallization and melt at 182° to 183°.

I. 0.2145 gram salt gave 0.0075 gram H_2O.
II. 0.2027 gram salt gave 0.0070 gram H_2O.

	Calculated for $Ca(C_{12}H_{23}O_2)_2 + H_2O$.	Found. I.	II.
H_2O	3.94	3.49	3.45

This salt is efflorescent, and this fact accounts for the somewhat low results obtained in the determination of water of crystallization.

I. 0.2070 gram anhydrous salt gave 0.0657 gram $CaSO_4$.
II. 0.1957 gram anhydrous salt gave 0.0613 gram $CaSO_4$.

	Calculated for $Ca(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Ca	9.12	9.33	9.21

Acid Magnesium Laurate, $Mg(C_{12}H_{23}O_2)_2.C_{12}H_{24}O_2$.—This salt was obtained by treating a hot alcoholic solution of lauric acid with a hot neutral alcoholic solution of magnesium acetate. It was expected that the normal magnesium laurate would be formed, but in two instances the acid salt was obtained, and it was impossible to obtain the normal salt. This

case of magnesium forming an acid salt seems to be an isolated one. The salt is the most soluble salt of lauric acid, with the exception of potassium and sodium laurates. It crystallizes most readily from 50 per cent alcohol in very fine, white needles, which melt at 74° to 75°. Analyses for magnesium gave the following results:

I. 0.2012 gram salt gave 0.0377 gram $MgSO_4$.
II. 0.2591 gram salt gave 0.0486 gram $MgSO_4$.

	Calculated for $Mg(C_{12}H_{23}O_2)_2.C_{12}H_{24}O_2$.	Found. I.	II.
Mg	3.91	3.79	3.79

Oudemans[1] described the normal magnesium laurate, $Mg(C_{12}H_{23}O_2)_2$, and said it contained 3 molecules of water of crystallization. Strange to say, this salt melted at 75°, the melting-point of the acid salt described above. Oudemans did not state how he prepared his magnesium laurate.

Zinc Laurate, $Zn(C_{12}H_{23}O_2)_2$.—Zinc laurate was made as the previous salts were. It is moderately soluble in alcohol, and crystallizes in delicate white needles, arranged in the form of rosettes. It also has a pearly or satin luster like that of the barium salt.

I. 0.2067 gram salt gave 0.0365 gram ZnO.
II. 0.2209 gram salt gave 0.0388 gram ZnO.

	Calculated for $Zn(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Zn	14.09	14.18	14.07

This salt was dried in the air and contained no water of crystallization. Oudemans[2] describes a zinc laurate to which he gave the formula $Zn(C_{12}H_{23}O_2)_2 + H_2O(?)$. This melted at 80°. The salt described above melts at 127°.

Copper Laurate, $Cu(C_{12}H_{23}O_2)_2$.—Copper laurate was made just as the previously described salts were. It separates as a light bluish-green, microscopically crystalline powder. It is very difficultly soluble in alcohol and insoluble in water. When heated, it gradually turns darker, and finally assumes a dark green color.

[1] *Loc. cit.*
[2] *Loc. cit.*

I. 0.2048 gram salt gave 0.0349 gram CuO.
II. 0.2110 gram salt gave 0.0359 gram CuO.

	Calculated for $Cu(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Cu	13.76	13.62	13.59

Oudemans[1] described a copper laurate, $Cu(C_{12}H_{23}O_2)_2$, which he said melted at 90°, while the above-described salt does not melt when heated to 220°.

Lead Laurate, $Pb(C_{12}H_{23}O_2)_2$.—Lead laurate was made like the other salts. It is insoluble in water, but may be crystallized from alcohol. It crystallizes in delicate white needles, which have a pearly luster. They melt at 101°. Oudemans[2] described his lead laurate as being amorphous, while the salt here described forms definite crystals with comparatively little difficulty.

I. 0.2757 gram salt gave 0.1382 gram $PbSO_4$.
II. 0.2580 gram salt gave 0.1294 gram $PbSO_4$.

	Calculated for $Pb(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Pb	34.18	34.22	34.23

Manganese Laurate, $Mn(C_{12}H_{23}O_2)_2$.—Manganese laurate was prepared as the other salts were. It is insoluble in water, but is soluble in alcohol. It separates out from its solution as a very pale pink, microscopically crystalline powder. The crystal form could not be determined. It melts at 76°, and contains no water of crystallization. Oudemans[3] described a manganese laurate melting at 75°, and containing x molecules of water of crystallization.

I. 0.2202 gram salt gave 0.0724 gram $MnSO_4$.
II. 0.2327 gram salt gave 0.0761 gram $MnSO_4$.

	Calculated for $Mn(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Mn	12.13	11.97	11.91

Cobalt Laurate, $Co(C_{12}H_{23}O_2)_2 + H_2O$.—Cobalt laurate was made as the other salts were and is quite soluble in alcohol, but insoluble in water. It forms delicate, pale-red needles, which melt at 52°, and then assume a dark-violet color. The

[1] *Loc. cit.*
[2] *Loc. cit.*
[3] *Loc. cit.*

cobalt laurate described by Oudemans[1] contained one molecule of water of crystallization, but melted at 75°.

I. 0.2211 gram salt gave 0.0078 gram H_2O.
II. 0.2070 gram salt gave 0.0074 gram H_2O.

	Calculated for $Co(C_{12}H_{23}O_2)_2 + H_2O$.	Found. I.	II.
H_2O	3.79	3.53	3.57

I. 0.2133 gram anhydrous salt gave 0.0716 gram $CoSO_4$.
II. 0.1996 gram anhydrous salt gave 0.0666 gram $CoSO_4$.

	Calculated for $Co(C_{12}H_{23}O_2)_2$.	Found. I.	II.
Co	12.89	12.77	12.71

REPORT.

The Oxygen Bases.

In the conception of oxygen—or oxonium—bases, there has been presented to chemists the introduction to what promises to be one of the most interesting chapters in the history of chemical theory, as well as one which bids fair to be far-reaching in its consequences. It is the purpose of this paper to put together in the form of a review the principal contributions to the subject which have thus far appeared.

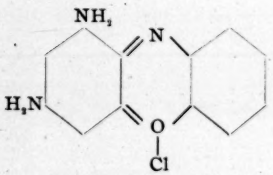
The conception was perhaps first hinted at by Mendeléeff as early as 1871, and was used by Friedel in 1875 to account for the compound of methyl ether with hydrochloric acid. He also used it to explain the suboxides of copper and silver, and considered it the basis of water of crystallization. Two years later van 't Hoff was led by the consideration of methyl ether to much the same conclusion, and in 1882 Armstrong expressed himself as a believer in the quadrivalence of oxygen. In 1888 Heyes[2] held that one of the oxygen atoms in the superoxides is quadrivalent, and ascribed the tendency to polymerization of aldehydes, cyanates, and other similar compounds to the same cause. A similar idea was used by Meldola, Schroeder, Brühl, and perhaps others, but it was not till 1899 that the conception of quadrivalent oxygen was forced upon chemists by experimental evidence.

In the summer of that year a paper was read by Collie and Tickle[3] before the Chemical Society of London on the salts of

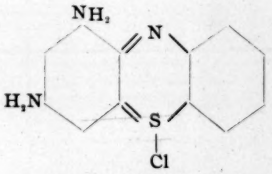
[1] *Loc. cit.*
[2] J. F. Heyes: The Tetravalence of Oxygen, Phil. Mag., [5], **25**, 221, 297 (1888).
[3] J. Chem. Soc. (London), **75**, 710 (1899).

dimethylpyrone. These salts are compared with those of dimethylpyridone, and the conclusion drawn that the oxygen atom in the pyrone must play the same part as the nitrogen atom in the pyridone. This assumes the quadrivalence of oxygen, and also that certain of its compounds have a basic character, due to its presence. Such compounds are analogous to the ammonium, phosphonium, sulphonium, and iodonium bases, and may be called oxonium bases. They are derivatives of the hypothetical oxonium hydroxide, OH_3OH. In favor of this hypothesis the authors mention the fact that ethers frequently form so-called double compounds with the halogen acids, such as dimethyl ether hydrochloride, diethyl ether hydriodide, and they also put in this category ethyl peroxide.

A few months later, a paper by Kehrmann[1] on the constitution of the oxazine dyestuffs was read before the German Chemical Society. In it the author makes use of the suggestion of Collie and Tickle to account for the structure of the diaminophenoxazine and diaminophenthiazine salts. The structure of these compounds would, therefore, be represented by the following :



Diaminophenazoxonium chloride.



Diaminophenazthionium chloride.

It is, of course, conceivable that it is the nitrogen atom, rather than the oxygen and the sulphur atom, which plays the part of the base, but a comparison of these compounds with diamidophenylphenazine as to color and absorption spectra seems to render this improbable. Several analogous azoxonium and azthionium salts have been described by Kehrmann[2] during the present year.

The contribution to this subject which has attracted the most wide-spread attention of chemists is the notable paper by Baeyer and Villiger,[3] on the basic properties of oxygen, which appeared in the *Berichte* for September 28th. After re-

[1] Ber. d. chem. Ges., **32**, 2601 (1899).
[2] *Ibid.*, **34**, 1623, 4170 (1901).
[3] *Ibid.*, **34**, 2679 (1901).

viewing various classes of compounds of oxygen which have been noted in the past as forming compounds with acids, which seem to be of the nature of salts, and referring to the work of Collie and Tickle, as being in every particular verified by them, they announce as a general proposition that the simple oxygen atom, in every form in which it appears throughout organic chemistry, is capable of forming salts; that not only in specially favorable circumstances, as Collie and Tickle thought, is it possible to obtain well-characterized salts, but with a few exceptions in every case provided only that the proper acids and the appropriate conditions are selected. The acids used in the preparation of the salts of Baeyer and Villiger were generally hydroferrocyanic, hydroferricyanic, and hydrocobalticyanic. In a few instances phosphotungstic and chlorplatinic acids were used. While a few oxygen compounds gave well-characterized salts with the simpler acids, in almost all cases far better and surer results were obtained with the complex acids. The cyanic acid reagents were prepared by precipitating the potassium salts with concentrated hydrochloric acid and filtering off the potassium chloride. Salts were formed with various members of the following classes of oxygen compounds: ethers, ethylene oxide, and cineol, primary, secondary, and tertiary alcohols, esters, aldehydes, ketones of all classes. No compounds with acids were obtained, though one of acetic acid is known. Perhaps the best results were obtained with cineol and with the ketones.

That these salts are not compounds of bivalent oxygen in the ordinary sense of the valence theory was shown by a careful study of the hydrochloride of dibenzalacetone, which is not a chlorhydrine of the formula

$$C_6H_5.CH : CH.C(OH)Cl.CH : CH.C_6H_5,$$

but has rather the formula

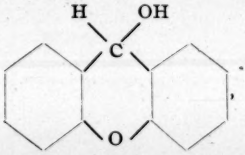
$$C_6H_5.CH : CH.\overset{\overset{HCl}{|}}{C}O.CH : CH.C_6H_5.$$

In favor of the theory that the oxygen bases are to be explained by the quadrivalence of oxygen, Baeyer cites the fact that the same influences which increase or diminish the basicity of nitrogen affect similarly the basicity of oxygen, and the same is true to a limited extent of sulphur. This is shown by the following table:

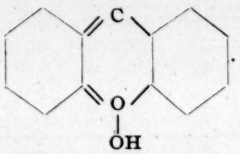
NH_3	OH_2	SH_2
base	neutral	acid
$N(C_2H_5)_3$	$O(C_2H_5)_2$	$S(C_2H_5)_2$
strong base	weak base	neutral
$N(C_2H_5)_4OH$	$O(C_2H_5)_3OH$	$S(C_2H_5)_3OH$
very strong base	hypothetical base	base

While the entrance of a positive group like alkyl renders the oxygen of the neutral water basic, this is not the case with negative groups like phenyl. Phenol, benzophenone, and similar compounds represent a class of oxygen compounds which form no salts. This is in complete accord with the character of nitrogen compounds, for in triphenylamine the basic quality of nitrogen has entirely disappeared. The basic character of oxygen is most noticeable in those compounds in which there is a double linkage between oxygen and carbon. This raises the question, which Baeyer does not attempt to answer, as to whether these compounds are not to be accounted for by the theory of residual affinity, using ideas which have been suggested by Armstrong,[1] Nef, Thiele, and others.

In the number of the *Berichte* following that in which Baeyer and Villiger's article appeared, Werner[2] takes up the work of Kehrmann, but develops it by avoiding the presence of nitrogen atoms in the molecule. The simplest compounds prepared were the perbromide and the ferric chloride double salt of xanthydrol, formed by the reduction of xanthone. Xanthydrol he considers to be a pseudoxanthoxonium base,

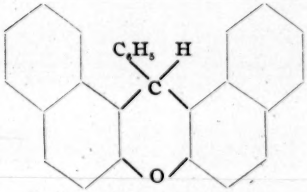


while its salts are derived from the true xanthoxonium base,

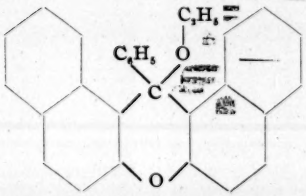


[1] Proc. Chem. Soc., 1901, 246.
[2] Ber. d. chem. Ges., 34, 3300 (1901).

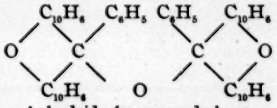
The compounds are better developed in the case of several analogous substances, which seem to leave little doubt of their structure, if they are to be accounted for by the valence theory. Such are the base formed by the reduction of benzal-β-dinaphthyl oxide, of which both the anhydride and the alcoholate of the pseudo base were formed, and the base from dixanthylene.



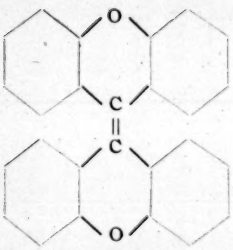
Benzal-β-dinaphthyl oxide.



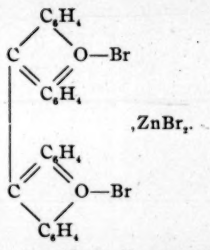
Alcoholate from pseudo base.



Anhydride from pseudo base.



Dixanthylene.



Zinc bromide double salt of dixanthoxonium bromide.

Werner also prepared similar derivatives containing sulphur in the place of oxygen and gives to these two classes the names of "carboxonium" and "carbothionium" salts. Werner looks upon the pyrone salts as being of analogous constitution, differing here somewhat from Baeyer and Collie.[1] According to Werner these are paraoxypyroxonium salts,

He also shows that pyrone itself is capable of forming salts.

In the same number of the *Berichte*, Rosenheim and Stellmann[2] describe a number of double compounds of antimony pentachloride, including several with different classes of oxygen compounds. Such are $SbCl_5,CH_3.CHO$, $SbCl_5,C_6H_5.CHO$, $SbCl_5,(CH_3)_2.CO$, $SbCl_5,C_6H_5,CO_2.C_2H_5$, $2SbCl_5,3C_6H_5.CO.Cl$, and $2SbCl_5,3CH_3CO.NH_2$. In the light of the oxygen bases these compounds possess a peculiar interest, especially in view of the fact that Rosenheim found that antimony chloride also forms double compounds with the organic acids, which is not the case with the complex inorganic acids with which Baeyer and Villiger worked.

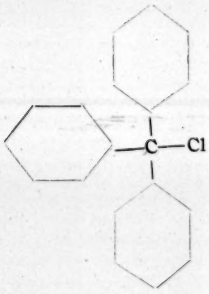
In the next number of the *Berichte*, Baeyer and Villiger[3]

[1] Ber. d. chem. Ges., **34**, 3612 (1901).

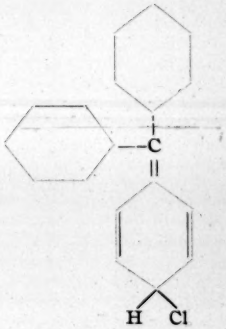
[2] *Ibid.*, **34**, 3377 (1901); Cf. also Rust: *Ibid.*, **30**, 2828 (1897).

take exception to the formula which Werner proposed for the pyrone salts, on the ground that there is no evidence of the presence of a hydroxyl group. He also expresses doubt as to whether the oxonium bases really correspond to the ammonium compounds, or are to be rather considered as molecular compounds. He calls attention to the resemblance which the salt-forming character of the oxygen compounds in general bears to that of the nitriles, which are ordinarily considered to have no basic properties. This is, however, not strictly the case, for the nitriles not only form compounds with tin tetrachloride and similar chlorides, but Baeyer shows that with the cyanic acids most of the nitriles tested form well-defined compounds which closely resemble those formed under similar circumstances with the oxygen compounds.

In a late number of the *Berichte*,[1] Kehrmann and Wentzel apply the ideas in the previous papers of Kehrmann to the constitution of Gomberg's triphenylmethyl, considering it as diphenylphenylenemethane, in which the para carbon atom of the phenylene group is bivalent, and like oxygen, under similar circumstances, plays the part of a base. When this carbon atom unites with the elements of hydrochloric acid, it becomes quadrivalent, and there is formed the isomeric yellow triphenylchlormethane. If this diagnosis is correct, we have here an instance of a 'carbonium' base.

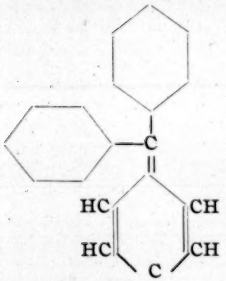


Colorless triphenylchlormethane.



Yellow triphenylchlormethane.

[1] Ber. d. chem. Ges., 34, 3815 (1901).



Gomberg's triphenylmethyl, a "carbonium" base.

In the same number of the *Berichte*, Hewitt[1] utilizes the oxonium theory as a prop to his theory of the cause of fluorescence.

Still more recently, Walker[2] has made an examination of dimethyl- and tetramethylpyrone by physico-chemical methods. Measuring their catalyzing effect upon methyl acetate, he finds that their basicity is practically the same as that of urea, dimethylpyrone being a little stronger base and tetramethylpyrone a little weaker. He also finds that the hydrochlorides of these compounds are hydrolyzed in aqueous solution to about the same extent as the hydrochloride of urea. He further shows, however, that, contrary to the statement of many text-books, ethylene oxide is by no means a strong base, but that its property of precipitating iron, aluminium, and magnesium hydroxides from solutions of their chlorides is due to the tendency of these salts to hydrolysis in aqueous solution.

Of the latest contributions to the subject, the most important is that of Walden,[3] who, after a historical review of the earlier work, gives the results of a series of physico-chemical experiments upon dimethylpyrone. (1) Violuric acid dissolved in a solution of dimethylpyrone shows no immediate increase of colored ions, showing that in this case dimethylpyrone has no decided tendency to form a salt, or that its salt with violuric acid is completely hydrolyzed. (2) From the influence of dimethylpyrone upon the birotation of grape-sugar, it appears that, if basic at all, it is a decidedly

[1] Ber. d. chem. Ges., **34**, 3819 (1901).
[2] *Ibid.*, **34**, 4115 (1901).
[3] *Ibid.*, **34**, 4185 (1901).

weaker base than aniline. (3) From the distribution coefficient of dimethylpyrone between water and benzene it appears that the picrate exists in concentrated aqueous solution, but is easily decomposed on dilution, even in the presence of an excess of the dimethylpyrone. (4) From the depression of the freezing-point the dissociation of dimethylpyrone is somewhat greater than that of pure water, that is, it is a somewhat stronger base than water. (5) In solution in liquid sulphur dioxide, dimethylpyrone is a relatively good electrolyte, corresponding in this particular to the tertiary nitrogen bases in the same solution. In acetonitrile it is an exceedingly weak electrolyte, but in the presence of tribromacetic acid, which likewise conducts very poorly, the solution increases decidedly in conductivity. This must be due to the formation of a salt. In water dimethylpyrone is a very poor conductor, and comparison shows that it is a weaker base than aniline but a stronger base than urea.

Conductivity experiments with dimethylpyrone and sodium hydroxide show that it is an amphoteric electrolyte, and the conclusion is drawn that this compound is in fact also a weak acid, capable of forming hydrogen ions as well as hydroxyl ions. In closing, Walden calls attention to the fact that oxygen must now be added to the long list of amphoteric elements, which are capable of forming both acids and bases, and suggests a similar possibility in the case of the halogens, as may be true with hypochlorous acid, which, while not conducting electricity, nevertheless forms salts with bases and reacts with acids.

From its first inception the theory of valence has undergone successive modifications and developments which have left it to-day very unlike the early conception. Regarding some of the elements, we have come to admit that they can have almost any valence, according to circumstances. Such is the case with manganese and ruthenium. In other cases we try to adhere to the idea of perissads and artiads, though here, as in the instance of sulphur and the halogens, we must admit an occasional exception. In a few cases, as hydrogen, the alkali metals, oxygen, and carbon, valence has been regarded as fixed, although there are a few notable stumbling blocks, such as carbon monoxide. Given any desired flexibility to the valence theory, it is, of course, possible to account for the structure of any compound.

But with all its changes and developments, our views of valence are far from flexible. We do not give up a single one of our valence ideas without a struggle. The quadrivalence and sexivalence of sulphur, the quinquivalence of nitrogen

were only accepted after a prolonged contest. The idea of the quadrivalence of oxygen is logical, is thoroughly in harmony with the properties of the oxygen group, and yet it will be generally accepted by chemists only when it is recognized as being the only possible way of accounting for many different compounds.

We cling to the theory of valence because we recognize that there is truth in it, but at the same time we recognize its insufficiency by making only a limited use of it. It accounts satisfactorily for the structure of most of our simpler compounds, it has been a wonderful and tolerably safe guide in the domain of organic chemistry, yet even in these two cases it is applicable with strictness only to gases where we know the weight of the molecule. In liquids we cannot be sure of it; in solution we know not what becomes of it when the ions are dissociated; in solids we can use it only by analogy. It is in solids, too, that the conception of valence most conspicuously breaks down. Between ammonium salts, double salts, such stable compounds as the platinum tetrammine bases, and the efflorescent decahydrate of sodium carbonate, we can bridge every step with intermediate compounds. In a limited field valence represents a quantitative truth; in a larger field it is like a scaffold, which more or less closely keeps to the outline of the structure, and is correspondingly useful didactically in gaining a conception of the structure itself. We are yet lacking in knowledge of the chemical affinity of the atom from a quantitative standpoint.

The importance of the oxygen bases does not lie in the question of the possible quadrivalence of the oxygen atom, but rather in that oxygen is brought still more closely into line with nitrogen, phosphorus, sulphur, and iodine in the development of base-forming properties, when united to negative organic groups.

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LEXINGTON, VA.,
DEC. 30, 1901.